

United States Patent

Cole

[15] 3,635,707

[45] Jan. 18, 1972

[54] **DIFFUSION TRANSFER PRODUCTS ADAPTED FOR MULTIPLE APPLICATION OF PROCESSING COMPOSITION AND/OR OPACIFIER AND PROCESSES FOR THEIR USE**

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[51] Int. Cl.....G03c 1/48, G03c 5/54, G03c 7/00

[58] Field of Search96/3, 76 C, 29 D

[56] References Cited

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2,607,685 8/1952 Land.....96/29 D

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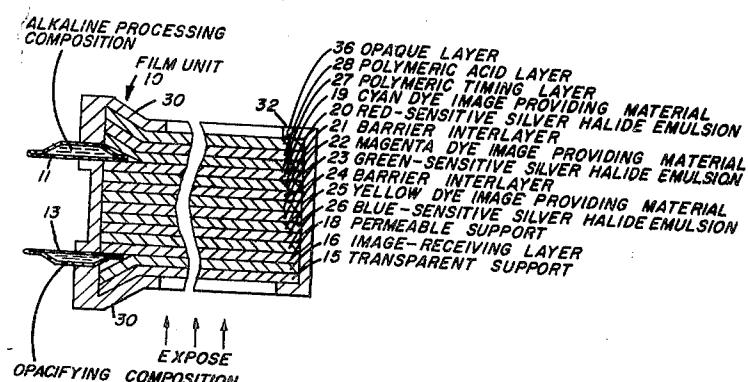
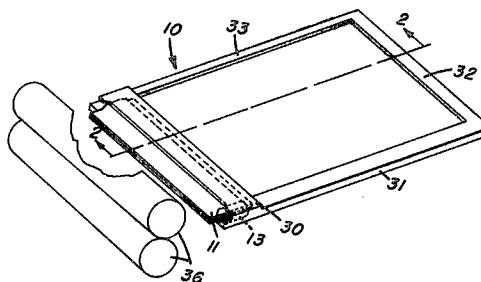
Attorney—W. H. J. Kline, J. R. Frederick and Harold E. Cole

[57] ABSTRACT

An integral negative-receiver film unit is disclosed which is

adapted for one-step processing. The film unit comprises a transparent support coated with an image-receiving layer and having thereon a photosensitive element comprising at least one, and preferably three, silver halide emulsion layers having associated therewith nondiffusible dye image-providing materials capable of reacting with oxidized developing agent to produce diffusible dyes, and a top sheet which can be transparent or opaque. Two rupturable containers or one container with two compartments containing either a processing composition or an opacifier or both are positioned (a) adjacent the top layer of the photosensitive element and sheet and (b) adjacent the image-receiving layer or a contiguous reflective layer and the bottom layer of the photosensitive element. The film unit is placed in a camera, exposed and then passed between a pair of pressure-applying members in the camera as it is being removed therefrom. The pressure-applying members rupture the containers and spread processing composition and/or opacifier over and underneath the photosensitive element to render it light insensitive. The processing composition develops the exposed silver halide layers and diffusible dye images are formed as a result of development which diffuse to the image-receiving layer to provide a positive, right-reading image which is viewed through the transparent support on an opaque reflecting layer background which is present initially in the film unit or formed by opacifier in a rupturable container. Several embodiments of the film unit may be interchangeably employed cameras either with or without an image-reversing optical system.

65 Claims, 6 Drawing Figures



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SHEET 1 OF 2

FIG. 1

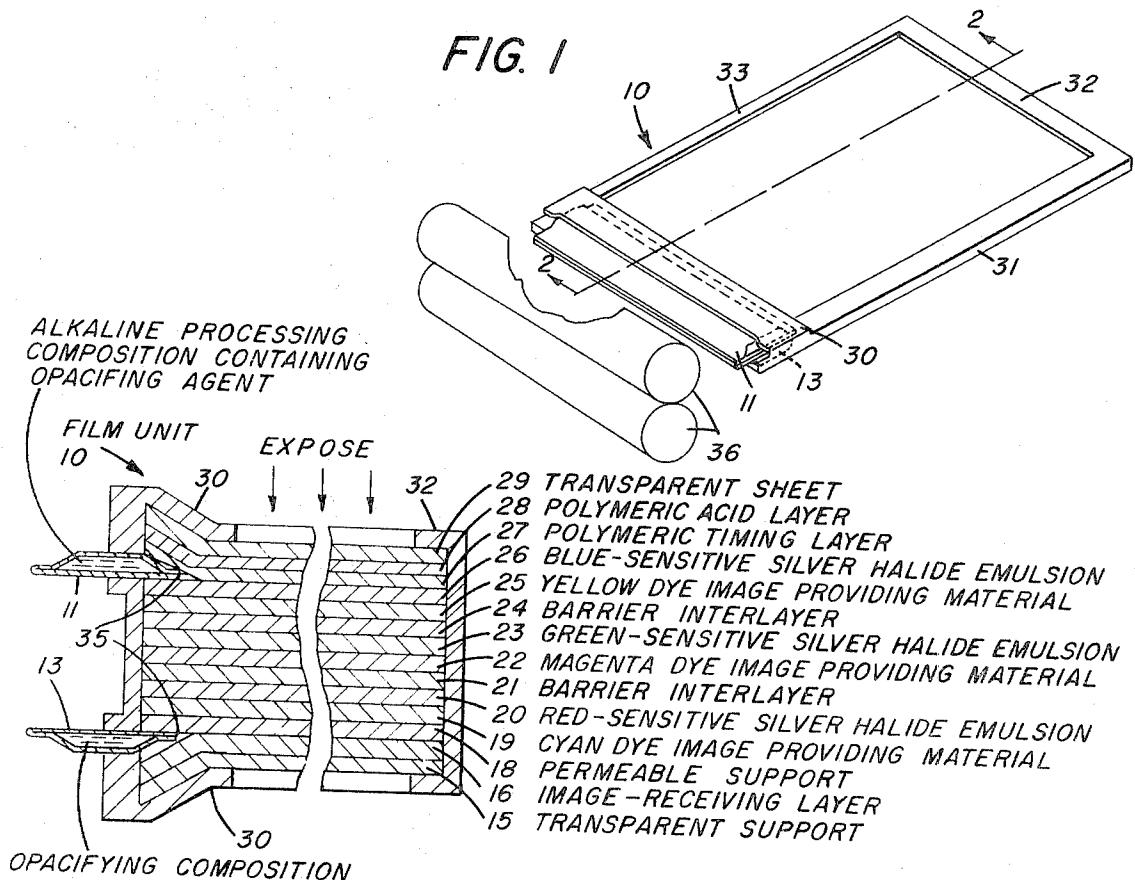
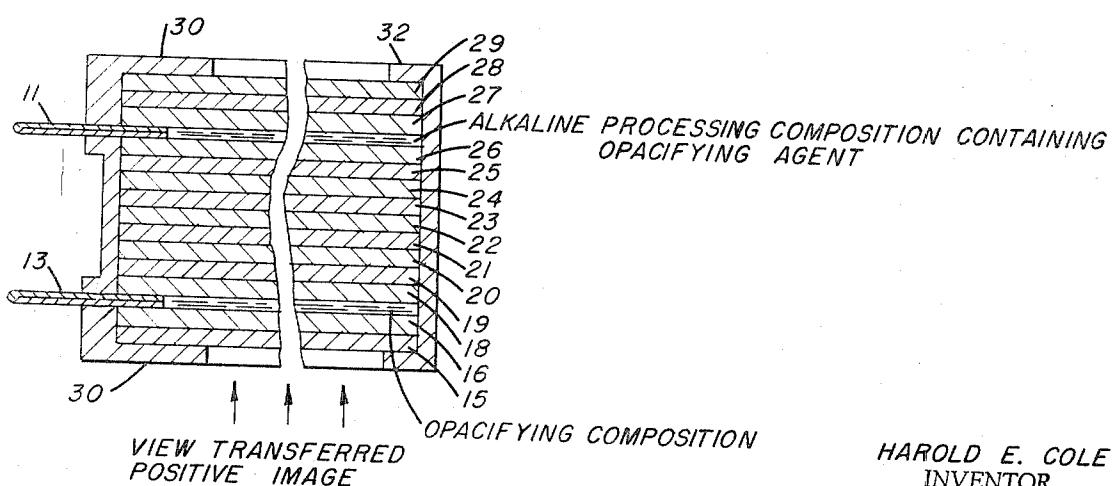


FIG. 2



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FIG. 3

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SHEET 2 OF 2

OPACIFYING COMPOSITION

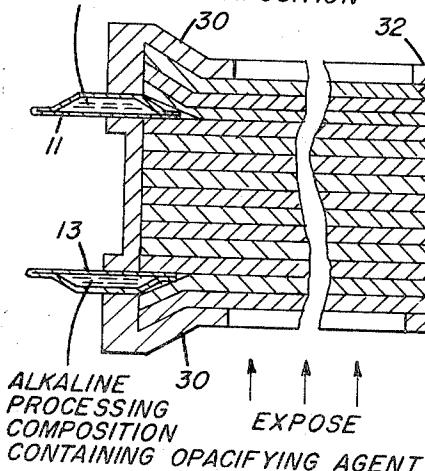


FIG. 4

- 29 TRANSPARENT SHEET
- 28 POLYMERIC ACID LAYER
- 27 POLYMERIC TIMING LAYER
- 19 CYAN DYE IMAGE PROVIDING MATERIAL
- 20 RED-SENSITIVE SILVER HALIDE EMULSION
- 21 BARRIER INTERLAYER
- 22 MAGENTA DYE IMAGE PROVIDING MATERIAL
- 23 GREEN-SENSITIVE SILVER HALIDE EMULSION
- 24 BARRIER INTERLAYER
- 25 YELLOW DYE IMAGE PROVIDING MATERIAL
- 26 BLUE-SENSITIVE SILVER HALIDE EMULSION
- 18 PERMEABLE SUPPORT
- 16 IMAGE-RECEIVING LAYER
- 15 TRANSPARENT SUPPORT

ALKALINE
PROCESSING
COMPOSITION
CONTAINING OPACIFYING AGENT

OPACIFYING COMPOSITION

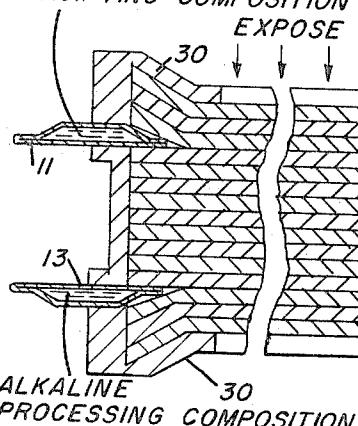


FIG. 5

- 29 TRANSPARENT SHEET
- 28 POLYMERIC ACID LAYER
- 27 POLYMERIC TIMING LAYER
- 26 BLUE-SENSITIVE SILVER HALIDE EMULSION
- 25 YELLOW DYE IMAGE PROVIDING MATERIAL
- 24 BARRIER INTERLAYER
- 23 GREEN-SENSITIVE SILVER HALIDE EMULSION
- 22 MAGENTA DYE IMAGE PROVIDING MATERIAL
- 21 BARRIER INTERLAYER
- 20 RED-SENSITIVE SILVER HALIDE EMULSION
- 19 CYAN DYE IMAGE PROVIDING MATERIAL
- 18 PERMEABLE SUPPORT
- 17 OPAQUE REFLECTIVE LAYER
- 16 IMAGE-RECEIVING LAYER
- 15 TRANSPARENT SUPPORT

ALKALINE PROCESSING
COMPOSITION

FILM UNIT

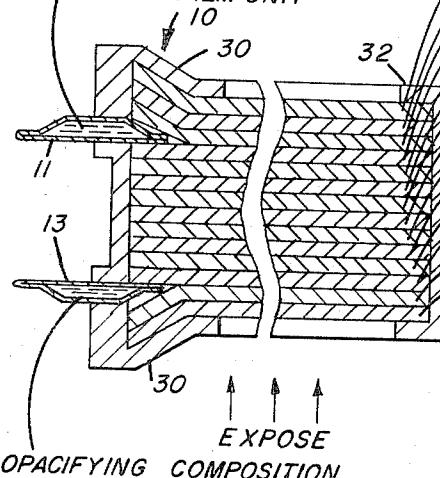


FIG. 6

- 36 OPAQUE LAYER
- 28 POLYMERIC ACID LAYER
- 27 POLYMERIC TIMING LAYER
- 19 CYAN DYE IMAGE PROVIDING MATERIAL
- 20 RED-SENSITIVE SILVER HALIDE EMULSION
- 21 BARRIER INTERLAYER
- 22 MAGENTA DYE IMAGE PROVIDING MATERIAL
- 23 GREEN-SENSITIVE SILVER HALIDE EMULSION
- 24 BARRIER INTERLAYER
- 25 YELLOW DYE IMAGE PROVIDING MATERIAL
- 26 BLUE-SENSITIVE SILVER HALIDE EMULSION
- 18 PERMEABLE SUPPORT
- 16 IMAGE-RECEIVING LAYER
- 15 TRANSPARENT SUPPORT

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DIFFUSION TRANSFER PRODUCTS ADAPTED FOR
MULTIPLE APPLICATION OF PROCESSING
COMPOSITION AND/OR OPACIFIER AND PROCESSES
FOR THEIR USE

This invention relates to photography and more particularly to an integral, negative-receiver color diffusion transfer film assembly, which can be exposed in a camera and processed outside the camera to yield a right-reading positive image.

Prior art U.S. Pat. No. 3,415,644; 3,415,645; and 3,415,646 described film assemblies designed for image transfer in which the receiving layer is not separated from the photosensitive element after processing which takes place out of the camera in room light. In order to obtain a right-reading positive, these prior art film assemblies require either an image-reversing optical system in the camera or require that an opaque sheet be placed over the top of the assembly after exposure and prior to removing the film assembly from the camera for processing.

It is an object of my invention to provide a novel film assembly which does not require an image-reversing optical system in a camera in order to obtain a right-reading positive, thus enabling the camera to employ a conventional optical system, to be less expensive and be less bulky, but which can in several embodiments be interchangeably employed in such cameras, if desired.

Another object of my invention is to provide a novel film assembly which does not require an in-camera lamination of an opaque sheet to the film assembly after exposure in order to obtain room light processing capability, thus enabling the camera to be less expensive and less bulky.

Another object of my invention is to provide a novel film assembly which can be exposed in a camera, processed outside the camera in room light to yield a right-reading positive image, and which does not require timing of development or any stripping away of the receiving layer from the negative portion of the photosensitive element after processing.

Still another object of my invention is to provide new processes for obtaining transfer images employing the novel film assemblies described herein.

These and other objects are obtained by the photographic film unit of my invention which is adapted to be processed by passing the unit between a pair of juxtaposed pressure-applying members and which comprises:

- a. a transparent support coated with an image-receiving layer having thereon a photosensitive element comprising at least one photosensitive silver halide emulsion layer, each said silver halide emulsion layer having associated therewith a nondiffusible dye image-providing material capable of reacting with oxidized developing agent to produce a diffusible dye;
- b. a top sheet superposed over the outermost layer of the photosensitive element from the transparent support;
- c. a first rupturable container being so positioned during processing, preferably transverse a leading edge of the photosensitive element, that a compressive force applied to the first container by the pressure-applying members will effect a discharge of the first container's contents between the top sheet and the outermost layer of the photosensitive element; and
- d. a second rupturable container being so positioned during processing, preferably transverse a leading edge of the photosensitive element, that a compressive force applied to the second container by the pressure-applying members will effect a discharge of the second container's contents between the image-receiving layer and the innermost layer of the photosensitive element from the transparent support;

the film unit containing a developing agent, one of the rupturable containers containing an opacifying agent, and the other rupturable container containing an alkaline processing composition.

In accordance with a first embodiment of my invention, the top sheet is transparent, the first rupturable container contains an alkaline processing composition having therein an opacify-

ing agent and the second rupturable container contains an opacifying agent.

In accordance with a second embodiment of my invention, the top sheet is transparent, the first rupturable container contains an opacifying agent and the second rupturable container contains an alkaline processing composition having therein an opacifying agent.

In accordance with a third embodiment of my invention, the top sheet is transparent, the first rupturable container contains an opacifying agent, the second rupturable container contains an alkaline processing composition, and the film unit contains an opaque reflecting layer intermediate the image-receiving layer and the photosensitive element.

In accordance with a fourth embodiment of my invention, the top sheet is opaque, the first rupturable container contains an alkaline processing composition and the second rupturable container contains an opacifying agent.

In using the various embodiments of the film assembly of this invention, the photosensitive unit is placed in a camera, exposed, and then passed between pressure-applying members in the camera as the unit is being removed therefrom. This compressive force breaks open the rupturable containers and spreads opacifying agent and processing composition into the film unit.

The negative portion of the film assembly will then be surrounded by opaque material to render it light insensitive, thus enabling the assembly to be removed from the camera during development. The processing composition diffuses through the film unit to either effect or initiate imagewise development of the silver halide emulsion layers. Imagewise distributions of diffusible dye image-providing material which is contained in each silver halide emulsion layer or in a layer contiguous thereto, are formed as a function of the imagewise exposure of each said silver halide emulsion layer. At least a portion of the imagewise distributions of diffusible dye image-providing material diffuse to the image-receiving layer to produce a positive dye image which can be viewed through the transparent support layer. The receiver portion of the film unit does not have to be stripped away from

the rest of the film unit and no timing of development is required.

Exposure and removal of the film assembly of my invention from a camera can be accomplished in a matter of seconds, thus freeing the camera for use in taking another photograph.

Whereas prior art film assemblies require relatively expensive, bulky cameras, with obvious disadvantages, for providing within the camera a mechanical film-handling system to manipulate the film after exposure to laminate an opaque sheet over the top prior to removing the film unit from the camera for processing, the film assembly of my invention can be employed in a very simple, inexpensive camera in which the only film movement in the camera after exposure occurs when the film unit passes between a pair of pressure-applying rollers as it is being removed from the camera. For example, the film assembly of my invention could be employed in a camera having the film-handling mechanism similar to that illustrated in U.S. Pat. No. 3,447,437, either with or without the image-reversing optical system illustrated in that patent, depending upon the particular embodiment employed. The ability to interchange film units of my invention with prior art film units for use in cameras either with or without an image-reversing optical system is an important aspect of this invention.

FIG. 1 is a perspective view of a first embodiment of a film unit according to the invention.

FIG. 2 and FIG. 3 are diagrammatic cross-sectional views of the film unit of FIG. 1 along section line 2-2, illustrating the various elements of a typical film unit before and after rupture of the rupturable containers or pods, the thickness of the various components being exaggerated for purposes of illustration.

FIG. 4, FIG. 5, and FIG. 6 are diagrammatic cross-sectional views of a second, third and fourth embodiment, respectively, of typical film units according to my invention.

The film assembly of my invention can be used to produce positive images in single or multicolors. In a three-color system, each silver halide emulsion layer of the film assembly of my invention will have associated therewith a dye image-providing material possessing a spectral absorption range substantially complementary to the predominant sensitivity range of its associated emulsion, i.e., the blue-sensitive silver halide emulsion layer will have a yellow dye image-providing material associated therewith, the green-sensitive silver halide emulsion layer will have a magenta dye image-providing material associated therewith, and the red-sensitive silver halide emulsion layer will have a cyan dye image-providing material associated therewith. The dye image-providing material associated with each silver halide emulsion layer may be contained either in the silver halide emulsion layer itself or in a layer contiguous to the silver halide emulsion layer.

Spectral sensitizing dyes can be used conveniently to confer additional sensitivity to the light sensitive silver halide emulsion of the multilayer photographic elements of the invention. For instance, additional spectral sensitization can be obtained by treating the emulsion with a solution of a sensitizing dye in an organic solvent or the dye may be added in the form of a dispersion as described in Owens et al. British Pat. No. 1,154,781. For optimum results, the dye can either be added to the emulsion as a final step or at some earlier stage.

Sensitizing dyes useful in sensitizing such emulsions are described, for example, in Brooker et al. U.S. Pat. No. 2,526,632; issued Oct. 24, 1950; Sprague U.S. Pat. No. 2,503,776; issued Apr. 11, 1950; Brooker et al. U.S. Pat. No. 2,493,748; and Taber et al. U.S. Pat. No. 3,384,486. Spectral sensitizers which can be used include the cyanines, merocyanines, complex (tri- or tetrานuclear) merocyanines, complex (tri- or tetrานuclear) cyanines, homopolar cyanines, styryls, hemicyanines (e.g., enamine hemicyanines), oxonols and hemoxonols. Dyes of the cyanine classes can contain such basic nuclei as the thiazolines, oxazolines, pyrrolines, pyridines, oxazoles, thiazoles, selenazoles and imidazoles. Such nuclei can contain alkyl, alkylene, hydroxyalkyl, sulfoalkyl, carboxyalkyl, aminoalkyl and enamine groups and can be fused to carbocyclic or heterocyclic ring systems either unsubstituted or substituted with halogen, phenyl, alkyl, haloalkyl, cyano, or alkoxy groups. The dyes can be symmetrical or unsymmetrical and can contain alkyl, phenyl, enamine or heterocyclic substituents on the methine or polymethine chain. The merocyanine dyes can contain the basic nuclei mentioned above as well as acid nuclei such as thiohydantoins, rhodanines, oxazolidenediones, thiazolidenediones, barbituric acids, thiazolineones, and malononitrile. These acid nuclei can be substituted with alkyl, alkylene, phenyl, carboxyalkyl, sulfoalkyl, hydroxyalkyl, alkoxyalkyl, alkylamino groups, or heterocyclic nuclei. Combinations of these dyes can be used, if desired. In addition, supersensitizing addenda which do not absorb visible light can be included, for instance, ascorbic acid derivatives, azaindenes, cadmium salts, and organic sulfonic acids as described in McFall et al. U.S. Pat. No. 2,933,390 and Jones et al. U.S. Pat. No. 2,937,089.

The various silver halide emulsion layers of a color film assembly of the invention can be disposed in the usual order, i.e., the blue-sensitive silver halide emulsion layer first with respect to the exposure side, followed by the green-sensitive and red-sensitive silver halide emulsion layers as shown in the drawing. If desired, a yellow dye layer or a Carey Lea silver layer can be present between the blue-sensitive and green-sensitive silver halide emulsion layer for absorbing or filtering blue radiation that may be transmitted through the blue-sensitive layer. If desired, the selectively sensitized silver halide emulsion layers can be disposed in a different order, e.g., the blue-sensitive layer first with respect to the exposure side, followed by the red-sensitive and green-sensitive layers.

The silver halide emulsions used in this invention can comprise, for example, silver chloride, silver bromide, silver chlorobromide, silver bromoiodide, silver chlorobromoiodide or mixtures thereof. The emulsions can be coarse or fine grain

and can be prepared by any of the well-known procedures, e.g., single jet emulsions, double jet emulsions, such as Lippmann emulsions, ammoniacal emulsions, thiocyanate or thioether ripened emulsions such as those described in Nietz et al. U.S. Pat. No. 2,222,264; Illingsworth U.S. Pat. No. 3,320,069; and McBride U.S. Pat. No. 3,271,157. Emulsions that contain silver halide grains having substantial surface sensitivity can be used, and emulsions that contain silver halide grains having substantial sensitivity inside the grains can be used as those described in Davey et al. U.S. Pat. No. 2,592,250; Porter et al. U.S. Pat. No. 3,206,313; and Bacon et al. U.S. Pat. No. 3,447,927. The emulsions can be regular grain emulsions such as the type described in Klein and Moisar, *J. Phot. Sci.*, Vol. 12, No. 5, Sept./Oct., 1964 pp. 242-251. Negative-type emulsions can be used or direct positive emulsions can be used such as those described in Leermakers U.S. Pat. No. 2,184,013; Kendall et al. U.S. Pat. No. 2,541,472; Berriman U.S. Pat. No. 3,367,778; Schouwenaars British Pat. No. 723,019; Illingsworth et al. French Pat. No. 1,520,821; Ives U.S. Pat. No. 2,563,785; Knott et al. U.S. Pat. No. 2,456,953 and Land U.S. Pat. No. 2,861,885.

The emulsions used in this invention can be sensitized with chemical sensitizers, such as with reducing agents; sulfur 25 selenium or tellurium compounds; gold, platinum or palladium compounds; or combinations of these. Suitable procedures are described in Sheppard et al. U.S. Pat. No. 1,623,499; Waller et al. U.S. Pat. No. 2,399,083; McVeigh U.S. Pat. No. 3,297,447; and Dunn U.S. Pat. No. 3,297,446.

The silver halide emulsions used in this invention may contain speed increasing compounds such as polyalkylene glycols, cationic surface active agents and thioethers or combinations of these as described in Piper U.S. Pat. No. 2,886,437; Dann et al. U.S. Pat. No. 3,046,134; Carroll et al. U.S. Pat. No. 3,294,900; and Goffe U.S. Pat. No. 3,294,540.

The silver halide emulsions used in the practice of this invention can be protected against the production of fog and can be stabilized against loss of sensitivity during keeping. Suitable antifoggants and stabilizers each used alone or in 40 combination include thiazolium salts described in Brooker et al. U.S. Pat. No. 2,131,038 and Allen et al. U.S. Pat. No. 2,694,716; the azaindenes described in Piper U.S. Pat. No. 2,886,437 and Heimbach et al. U.S. Pat. No. 2,444,605; the mercury salts as described in Allen et al. U.S. Pat. No. 2,728,663; the urazoles described in Anderson et al. U.S. Pat. No. 3,287,135; the sulfocatechols described in Kennard et al. U.S. Pat. No. 3,236,652; the oximes described in Carroll et al. British Pat. No. 623,448; nitron; nitroindazoles; the mercaptotetrazoles described in Kendall et al. U.S. Pat. No. 2,403,927; Kennard et al. U.S. Pat. No. 3,266,897 and Luckey et al. U.S. Pat. No. 3,397,987; the polyvalent metal salts described in Jones U.S. Pat. No. 2,839,405; the thiuronium salts described in Herz et al. U.S. Pat. No. 3,220,839; and the palladium, platinum and gold salts described in Trivelli et al. U.S. Pat. No. 2,566,263 and Yutzy et al. U.S. Pat. No. 2,597,915.

The dye image-providing material associated with each silver halide emulsion layer in this invention can be any 60 material which is nondiffusing in alkaline processing compositions and in photographic silver halide emulsions but which produces a diffusible dye on reaction with oxidized silver halide photographic developing agents. Preferably the dye image-providing material is a nondiffusible coupler which 65 produces a diffusible dye on reaction with oxidized aromatic primary amino color developing agents such as p-phenylenediamine developing agents. Such nondiffusible couplers may be employed in layer arrangements in a photosensitive element which have advantages over other dye image-providing materials. For example, in a system employing an initially 70 soluble and diffusible dye image-providing material such as a dye developer, unless the dye developer is chromatically shifted (which is a technically difficult task to obtain three such compounds which will not absorb blue, green and red light, respectively, during exposure, and which will form yet-

low, magenta and cyan dyes, respectively, after transfer), it will usually have to be employed in a layer underneath a contiguous photosensitive silver halide emulsion layer with respect to the exposure side so that exposure and diffusion of unoxidized dye developer take place in opposite directions in order to obtain optimum photographic speed and monitoring of the dye developer layer by the exposed silver halide emulsion layer. If the dye developer layer were not underneath its contiguous photosensitive silver halide emulsion layer with respect to the exposure side, then it would act as a filter layer which would decrease photographic speed and therefore would be undesirable. By employing nondiffusible couplers as the dye image-providing material, exposure and diffusion of the diffusible dye which is produced can take place in the same direction which provides a right-reading image on the image-receiving layer without the need for an image-reversing optical system or a stripping step to reverse the image. These advantages can be seen by comparing various embodiments of the invention described herein with typical integral systems which employ initially soluble and diffusible dye image-providing materials, such as dye developers, as described in U.S. Pat. Nos. 3,415,644; 3,415,645; 3,415,646; 3,473,925; Belgian Pat. No. 732,985 (corresponding to Rogers U.S. application Ser. Nos. 728,535 filed May 13, 1968 now abandoned and 815,585 filed Apr. 14, 1969 now abandoned); and U.S. Pat. No. 2,983,606, column 24, lines 57-73.

A system employing the nondiffusible couplers described herein also has many advantages over systems employing initially diffusible couplers. For example, it is not possible to obtain good color separation in an initially diffusible coupler system unless separate receiving sheets are assembled in register as described in U.S. Pat. No. 2,647,049 and 2,698,798, column 13, lines 64-85 or unless sequential transfers are made to a single receiver as described in U.S. Pat. No. 2,698,798, column 14, lines 1-12. These such systems, obviously, cannot be employed with a single developing composition and a single receiver as described by the invention herein to provide a high quality, multicolor, transfer image having good color separation and low D_{min} . In addition, initially diffusible coupler systems require the use of an oxidizing agent in the receiving layer to oxidize the transferred color developing agent which would tend to degrade the multicolor image or wander into other layers of the integral element causing color contamination.

The nondiffusible couplers of this invention include those having formulas:

DYE-LINK-(COUP-BALL)_n

and

BALL-LINK-(COUP-SOL)_n

wherein

1. DYE is a dye radical exhibiting selective absorption in the visible spectrum and containing an acidic solubilizing radical;

2. LINK is a connecting radical such as an azo radical, a mercuri radical, an oxy radical, an alkylidene radical, a thio radical, a dithio radical or an azoxy radical;

3. COUP is a coupler radical such as a 5-pyrazolone coupler radical, a pyrazolotriazole coupler radical, a phenolic coupler radical or an open-chain ketomethylene coupler radical, COUP being substituted in the coupling position with LINK;

4. BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render such coupler nondiffusible during development in the alkaline processing composition;

5. SOL is a hydrogen atom or an acidic solubilizing group when the color developing agent contains an acidic solubilizing group, and SOL is an acidic solubilizing group when the color developing agent is free of an acidic solubilizing group; and

6. n is an integer of 1 to 2 when LINK is an alkylidene radical, and n is 1 when LINK is an azo radical, a mercuri radical, an oxy radical, a thio radical, a dithio radical or an azoxy radical.

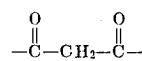
The acidic solubilizing radicals attached to the diffusible dye producing couplers described above can be solubilizing radicals which when attached to the coupler or developer moieties of the dyes, render the dyes diffusible in alkaline processing compositions. Typical of such radicals are carboxylic, sulfonic, ionizable sulfonamide, and hydroxy-substituted groups that lend to dyes negative charges.

The nature of the ballast groups in the diffusible dye-producing coupler compounds described above (BALL—) is

10 not critical as long as they confer nondiffusibility to the coupler compounds. Typical ballast groups include long chain alkyl radicals linked directly or indirectly to the coupler molecules as well as aromatic radicals of the benzene and naphthalene series, etc., linked directly or indirectly to the coupler molecules by a splittable linkage, or by a removable or irremovable but otherwise nonfunctional linkage depending upon the nature of the coupler compound. Useful ballast groups have at least eight carbon atoms.

15 20 Typical dye radical substituents (DYE—) include azo, azomethine, indoaniline, indophenol, anthraquinone and related dye radicals well known in the art that exhibit selective absorption in the visible spectrum. The dye radicals contain acidic solubilizing moieties.

25 30 With regard to the above-described coupler radicals (COUP—), the "coupling position" is well known to those skilled in the photographic art. The 5-pyrazolone coupler radicals couple at the carbon atom in the 4-position, the phenolic coupler radicals, including α -naphthols, couple at the carbon atom in the 4-position and the open-chain ketomethylene coupler radicals couple to the carbon atom forming the methylene moiety (e.g.,



35 * denoting the coupling position). Pyrazolotriazole couplers and their coupling position are described, for example, in U.S. Pat. No. 3,061,432 and U.S. application Ser. No. 778,329 of Bailey et al., filed Nov. 22, 1968.

40 45 Particularly good results are obtained when the cyan-producing coupler has the formula BALL—O—CYANCOUP, the magenta-producing coupler has the formula BALL—N=N—MAGCOUP and the yellow-producing coupler has the formula BALL—O—YELLCOUP wherein:

a. BALL is a photographically inert organic ballasting radical having at least eight carbon atoms and of such molecular size and configuration as to render the coupler nondiffusible during development in an alkaline processing composition;

b. CYANCOUP is a phenolic coupler radical substituted in the 2-position with a fully substituted amido group and attached to the —O— moiety of the cyan-producing coupler in the coupling position;

c. MAGCOUP is a 5-pyrazolone coupler radical joined to the —N=N— moiety of the magenta-producing coupler in the coupling position; and

d. YELLCOUP is an open-chain ketomethylene coupler radical attached to the —O— moiety of the yellow-producing coupler in the coupling position.

The term "nondiffusing" used herein as applied to the couplers, has the meaning commonly applied to the term in color photography and denotes materials which for all practical purposes do not migrate or wander through organic colloid layers, such as gelatin, comprising the sensitive elements of the invention. The same meaning is to be attached to the term "immobile."

65 70 75 The term "diffusible" as applied to the dyes formed from the "nondiffusing" couplers in this invention has the converse meaning and denotes materials having the property of diffusing effectively through the colloid layers of the sensitive elements in the presence of the "nondiffusing" materials from which they are derived. "Mobile" has the same meaning.

When the couplers having the formula DYE-LINK-(COUP-BALL)_n as described above are reacted with oxidized color developing agent, the connecting radical (LINK) is split and a diffusible preformed dye (DYE) is released which diffuses imagewise to a reception layer. An acidic solubilizing group on the preformed dye lends diffusibility to the dye molecule. The coupling portion of the coupler (COUP) couples with the color developing agent oxidation product to form a dye that is nondiffusible because of the attached ballasting group (BALL) in a noncoupling position. In this type of coupler, the color of the diffusible dye is determined by the color of the preformed dye moiety (DYE), the color of the reaction product of color developer oxidation product and the coupler moiety (COUP) being unimportant to the color of the diffusible image.

When couplers having the formula BALL-LINK-(COUP-SOL)_n as described above are reacted with oxidized color developing agent, the connecting radical (LINK) is split and a diffusible dye is formed with the color developing agent oxidation product and the coupling portion (COUP) of the coupler which diffuses imagewise to a reception layer. Diffusibility is imparted to the dye by an acidic solubilizing group attached to a noncoupling position of the coupling portion (COUP) of the coupler or to the color developing agent. The ballasting portion of the coupler remains immobile. In this type of coupler, the color of the diffusible dye is determined by the color of the reaction product of color developer oxidation product and the coupler moiety (COUP).

In using both types of couplers in the invention, the production of diffusible dye images is a function of the reduction of developable silver halide images which may involve direct or reversal development of the silver halide emulsions with an aromatic primary amino developing agent. If the silver halide emulsion employed is a direct positive silver halide emulsion, such as an internal image emulsion or a solarizing emulsion, which is developable in unexposed areas, a positive image can be obtained in the receiver portion of the film unit. In this embodiment, the nondiffusible coupler can be located in the silver halide emulsion itself. After exposure of the film unit, the alkaline processing composition permeates the various layers to initiate development of the exposed photosensitive silver halide emulsion layers. The aromatic primary amino color developing agent present in the film unit develops each of the silver halide emulsion layers in the unexposed areas (since the silver halide emulsions are direct positive ones), thus causing the developing agent to become oxidized imagewise corresponding to the unexposed areas of the direct positive silver halide emulsion layers. The oxidized developing agent then reacts with the nondiffusible coupler present in each silver halide emulsion layer to form imagewise distributions, respectively, of diffusible cyan, magenta and yellow dye as a function of the imagewise exposure of each of the silver halide emulsion layers. At least a portion of the imagewise distributions of diffusible cyan, magenta and yellow dye diffuse to the image-receiving layer to provide a positive dye image viewable through the transparent support. After being contacted by the alkaline processing composition, a pH-lowering layer in the film unit lowers the pH of the film unit to stabilize it. Since the receiving layer does not have to be stripped away from the negative portion of the film unit, the composite structure can be maintained intact subsequent to processing. Specific examples of such nondiffusing couplers and other details concerning this type of photographic chemistry are found in U.S. Pat. Nos. 3,227,550 and 3,227,552.

Internal image silver halide emulsions useful in the above-described embodiment are direct positive emulsions that form latent images predominantly inside the silver halide grains, as distinguished from silver halide grains that form latent images predominantly on the surface thereof. Such internal image emulsions were described by Davey et al. in U.S. Pat. No. 2,592,250 issued Apr. 8, 1952, and elsewhere in the literature. Internal image silver halide emulsions can be defined in terms of the increased maximum density obtained when developed

with "internal-type" developers over that obtained when developed with "surface-type" developers. Suitable internal image emulsions are those which, when measured according to normal photographic techniques by coating a test portion of the silver halide emulsion on a transparent support, exposing to a light intensity scale having a fixed time between 0.01 and 1 second, and developing for 3 minutes at 20° C. in Developer A below ("internal-type" developer), have a maximum density at least five times the maximum density obtained when an equally exposed silver halide emulsion is developed for 4 minutes at 20° C. in Developer B described below ("surface-type" developer).

DEVELOPER A

15	Hydroquinone	15 g.
	Monomethyl-p-aminophenol sulfate	15 g.
	Sodium sulfite (desiccated)	50 g.
	Potassium bromide	10 g.
20	Sodium hydroxide	25 g.
	Sodium thiosulfate	20
	Water to make 1 liter.	

DEVELOPER B

25	P-hydroxyphenylglycine	10
	Sodium carbonate	100 g.
	Water to make 1 liter	

The solarizing direct positive silver halide emulsions useful in the above-described embodiment are well-known silver halide emulsions which have been effectively fogged either chemically or by radiation to a point which corresponds approximately to the maximum density of the reversal curve as shown by Mees, *The Theory of the Photographic Process*, published by the MacMillan Co., New York, N.Y., 1942, pages 261-297. Typical methods for the preparation of solarizing emulsions are shown by Groves British Pat. No. 443,245, Feb. 25, 1936, who subjected emulsions to Roentgen rays "until an emulsion layer formed therefrom, when developed without preliminary exposure, is blackened up to the apex of its graduation curve"; Szaz British Pat. No. 462,730, Mar. 15, 1937, the use of either light or chemicals such as silver nitrate, organic sulfur compounds and dyes to convert ordinary silver halide emulsions to solarizing direct positive emulsions; and Arens U.S. Pat. No. 2,005,837, June 25, 1935, the use of silver nitrate and other compounds in conjunction with heat to effect solarization. Kendall and Hill U.S. Pat. No. 2,541,472, Feb. 13, 1951, shows useful solarized emulsions particularly susceptible to exposure with long wavelength light and initial development to produce the Herschel effect described by Mees above, produced by adding benzothiazoles and other compounds to the emulsions which are fogged either chemically or with white light. In using the emulsions a sufficient reversal image exposure is employed using minus blue light of from about 500-700 m μ wavelength preferably 520-554 m μ , to substantially destroy the latent image in the silver halide grains in the region of the image exposure. Particularly useful are the fogged direct positive emulsions of Berriman U.S. Pat. No. 3,367,778 and French Pat. No. 1,520,821.

Internal image silver halide emulsions which contain or which are processed in the presence of fogging or nucleating agents are particularly useful in the above-described embodiment employing nondiffusible couplers since the use of fogging agents is a convenient way to inject electrons into the silver halide grains. Suitable fogging agents include the hydrazines disclosed in Ives U.S. Pat. No. 2,588,982 issued Mar. 11, 1952 and No. 2,563,785 issued Aug. 7, 1951; the hydrazides and hydrazone disclosed in Whitmore U.S. Pat. No. 3,227,552 issued Jan. 4, 1966; hydrazone quaternary salts described in Lincoln and Heseltine application Ser. No. 828,064 filed Apr. 28, 1969, now abandoned; or mixtures thereof. The quantity of fogging agent employed can be widely varied depending upon the results desired. Generally, the concentration of fogging agent is from about 1 to about 20 mg.

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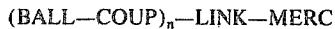
per square foot of photosensitive layer in the photosensitive element or from about 0.1 to about 2 grams per liter of developer if it is located in the developer.

Another embodiment of the invention employing the non-diffusible couplers described above to produce a diffusible dye image-providing material is to employ them in combination with development inhibitor-releasing couplers as described in U.S. Pat. No. 3,227,551. In such an embodiment, the photosensitive portion of the photosensitive element would comprise at least two Color-Forming Units in layers sensitive to different regions of the visible spectrum, separated by a barrier layer comprising a hydrophilic colloid containing a water-insoluble reactant capable of forming a water insoluble salt with mercaptans, each of the Color-Forming Units comprising:

1. a developable emulsion layer of a hydrophilic colloid and a water insoluble metal salt which is developable by an aromatic primary amino color developing agent to substantial density without exposure to light, the metal salt having contiguous thereto the nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to form a diffusible dye; and
2. a photosensitive silver halide emulsion layer, the silver halide of which has contiguous thereto a nondiffusible development inhibitor-releasing coupler which is capable of reacting with oxidized aromatic primary amino color developing agent to release a diffusible mercaptan development inhibitor which is capable of diffusing imagewise to the adjacent developable emulsion layer to inhibit development therein.

The aromatic primary amino color developing agent is preferably a p-phenylenediamine developing agent which is present in the alkaline processing composition and the developable emulsion is preferably an emulsion of a hydrophilic colloid, silver thiocyanate and physical development nuclei that can be developed to substantial density without exposure to light. The developable emulsion can also be made from a metal salt which is made spontaneously developable by incorporating in the emulsion a wide variety of well-known physical development nuclei as disclosed in the above-mentioned U.S. Pat. No. 3,227,551, column 6, lines 63-75 and column 7, lines 1-10. Another method that can be utilized to make the water-insoluble salts spontaneously developable is by prefogging the emulsion with light or with chemical reducing agents such as alkali metal borohydrides and the like in accordance with well-known photographic fogging techniques.

The development inhibitor-releasing couplers which can be employed in the above embodiment are those having the formula:



or



wherein:

1. BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render the coupler nondiffusible during development in the alkaline processing composition;
2. COUP is a coupler radical such as a 5-pyrazolone coupler radical, a phenolic coupler radical or an open-chain ketomethylene coupler radical, COUP being substituted in the coupling position with said LINK;
3. LINK is a connecting radical such as an azo radical, a mercuri radical, an oxy radical, an alkylidene radical, a thio radical, a dithio radical or an azoxy radical;
4. MERC is a diffusible radical containing a mercapto radical ($-SH$);
5. RAD is a photographically inert, diffusible radical that forms a mercaptan with the monothio connecting or linking radical ($-S-$);
6. n is an integer of 1 to 2 when LINK is an alkylidene radical and n is 1 when LINK is an azo radical, a mercuri radical, an oxy radical, a thio radical, a dithio radical or an azoxy radical; and
7. m is an integer of 0 or 1.

A wide variety of photographically inert radicals that are diffusible in the layers of the Color-Forming Unit and form mercaptans with the monothio connecting or linkage radical when the connecting is split on development can be used for the RAD substituent of the development inhibitor-releasing couplers. Typical of such radicals are aryl, alkaryl and carbon-containing heterocyclic radicals. The aryl moiety of such radicals is preferably phenyl, and includes such substituents as nitro, lower alkyl, lower alkylamido, lower alkoxy, lower alkylsulfoamido, lower alkylcarbamyl, carbon-containing heterocyclic radicals and the like. The carbon-containing heterocyclic radicals, which can be attached directly to the monothio linkage radical or as a substituent on the described aryl moieties, generally contain at least one hetero nitrogen, oxygen or sulfur atom, and preferably, one to four hetero nitrogen atoms. The hetero nitrogen atoms in the heterocyclic radicals have no hydrogen atom attached thereto as the RAD radical is photographically inert. Illustrative carbon-containing heterocyclic radicals include 1-phenyltetrazolyls, oxazolyls, oxadiazolyls, diazolyls, thiadiazolyls, benzoxazolyls, benzothiazolyls, pyrimidyls, pyridinyls, quinolinyls and the like.

MERC is a preformed mercapto development inhibiting moiety. A wide variety of diffusible radicals containing a mercapto radical ($-SH$) can be used for the MERC substituent of the development inhibitor-releasing couplers. The mercapto radical can be suitably attached to an aryl, alkaryl or a carbon-containing heterocyclic radical such as RAD described above except that it is not necessary that the hetero nitrogen atoms on the heterocyclic radicals be free of hydrogen atoms.

When development inhibitor-releasing couplers having the formula (BALL-COUP)_n-LINK-MERC are reacted with oxidized color developing agent, the connecting radical (LINK) is split and a mercaptan development inhibitor (MERC) is released that is diffusible in the Color-Forming Unit. A ballasted or immobile dye is formed by reacting the coupler moiety (COUP) at the coupling position with oxidized color developing agent. The connecting radical (LINK) is preferably an azo ($-N=N-$) or a monothio ($-S-$) radical in this type of development inhibitor-releasing coupler. As such development inhibitor-releasing couplers are preformed development inhibitors, they are preferably utilized in a layer adjacent to the light-sensitive silver halide emulsion layer of the present Color-Forming Units.

When development inhibitor-releasing couplers having the formula (BALL)_m-COUP-S-RAD are reacted with oxidized color developing agent, the thio connecting or linkage radical (S) is split from the coupling position of the coupler moiety (COUP) and a mercaptan development inhibitor is formed that is diffusible in the Color-Forming Unit. When m is one, a ballasted or immobile dye is formed by reacting the coupler moiety (COUP) at the coupling position with oxidized color developing agent. When m is zero, a nondiffusible or a nonmordantable dye is formed by reacting the coupler moiety (COUP) at the coupling position with oxidized color developing agent, both the development inhibitor-releasing coupler and the color developing agent being free of acidic solubilizing groups when m is zero and the dye formed is diffusible. The substituent m is preferably one, and such development inhibitor-releasing couplers can be utilized either in the light-sensitive emulsion or in a layer adjacent thereto in the present Color-Forming Units.

The nature of the ballast groups (BALL) in the development inhibitor-releasing coupler compounds described above is not critical as long as they confer nondiffusibility to the coupler compounds. Typical ballast groups include long-chain alkyl radicals or several short chain alkyl radicals having e.g., 8-22 carbon atoms, linked directly or indirectly to the coupler molecules, as well as aromatic radicals of the benzene and naphthalene series, etc., linked directly or indirectly to the coupler molecules by splittable linkage, or by a removable or irremovable but otherwise nonfunctional linkage depending upon the nature of the coupler compound. Useful ballast groups generally have at least eight carbon atoms.

In a color diffusion transfer system employing the above-described development inhibitor-releasing couplers and non-diffusible couplers, the Color-Forming Units are sensitive to blue, green and red light and are capable of forming imagewise distributions of diffusible yellow, magenta and cyan dyes. After exposure of the film unit, the alkaline processing composition permeates the various layers to initiate development of the latent image contained in each photosensitive silver halide emulsion layer. The aromatic primary amino color developing agent present in the film unit, preferably in the alkaline processing composition itself, develops each of the exposed silver halide emulsion layers, thus causing said aromatic primary amino color developing agent to become oxidized imagewise. The oxidized developing agent then reacts with the nondiffusible development inhibitor-releasing coupler contiguous to the silver halide emulsion layer to release a diffusible mercaptan development inhibitor. The mercaptan development inhibitor thereafter diffuses imagewise to each adjacent developable emulsion layer to inhibit development therein corresponding to areas of exposure of the photosensitive silver halide emulsion, the barrier layers preventing the mercaptan development inhibitor formed in one Color-Forming Unit from diffusing to another Color-Forming Unit by forming an insoluble salt with mercaptans diffusing to said barrier layers. The remaining areas of each developable emulsion layer wherein development has not been inhibited corresponding to the unexposed areas of the photosensitive silver halide emulsion, are thus developed spontaneously by the developing agent, thus causing the developing agent to become oxidized. The oxidized developing agent then reacts with the nondiffusible coupler contiguous to the metal salt in each developable emulsion layer to form imagewise distributions, respectively, of diffusible cyan, magenta and yellow dye as a function of the imagewise exposure of each silver halide emulsion layer. At least a portion of the imagewise distributions of diffusible cyan, magenta and yellow dye then diffuse to the image-receiving layer to provide a positive dye image viewable through the transparent support. After being contacted by the alkaline processing composition, a pH-lowering layer in the film unit lowers the pH of the film unit to stabilize it. Since the receiving layer does not have to be stripped away from the negative portion of the film unit, the composite structure can be maintained intact subsequent to processing.

The barrier layers referred to above are used between Color-Forming Unit to ensure that the activity of the mercaptan development inhibitor is confined to a single Color-Forming Unit. Hence, the barrier layers contain a water-insoluble salt or metal capable of forming a water-insoluble salt with mercaptans, silver halides such as silver chloride, silver bromide, silver iodide, silver bromoiodide, silver chlorobromoiodide, etc., being preferably used. Other compounds suitable for use include colloidal metals such as silver and gold; and colloidal metal sulfides, selenides and tellurides such as lead sulfide, nickel sulfide, cadmium sulfide, silver sulfide, copper sulfide, zinc sulfide, mercury sulfide, silver selenide, silver telluride and the like. The barrier layers containing light-sensitive silver salts are prepared to be substantially less sensitive to light than the light-sensitive emulsions in the Color-Forming Units. Such barrier layers also serve to prevent oxidized color developing agent from wandering from one Color-Forming Unit to another where it could cause color contamination. Antioxidants such as n-octadecyl hydroquinone and the like phenolic antioxidants, and nondiffusible photographic color couplers that form nondiffusible dyes on coupling with oxidized aromatic primary amino color developing agents can be utilized in the barrier layers to prevent wandering of such oxidized color developing agent.

Specific examples of the above-described mercaptan development inhibitor-releasing couplers and other details concerning this type of photographic chemistry are found in the above-mentioned U.S. Pat. No. 3,227,551.

Still another embodiment of the invention employing the nondiffusible couplers described above to produce a diffusible

75 dye image-providing material is to employ them in combination with physical development nuclei in a nuclei layer contiguous to each photosensitive silver halide emulsion layer. The film unit contains a silver halide solvent, preferably in a rupturable container with the alkaline processing composition, and each photosensitive silver halide emulsion layer contains an immobilizing coupler, e.g., a coupler with a ballast group, which is capable of reacting with oxidized aromatic primary amino color developing agent to form an immobile product. Each photosensitive silver halide emulsion layer and its contiguous nuclei layer are separated from the other silver halide emulsions and their contiguous nuclei layers in the film unit by means of an alkaline solution-permeable barrier layer for retaining silver complexes. After exposure of the film unit, the alkaline processing composition permeates the various layers to initiate development of the latent image contained in each photosensitive silver halide emulsion layer. The aromatic primary amino color developing agent present in the film unit develops each of the exposed silver halide emulsion layers, thus causing the aromatic primary amino color developing agent to become oxidized imagewise. The oxidized developing agent then reacts with the immobilizing coupler present in each said photosensitive silver halide emulsion layer to form an immobile product. The remaining silver halide in each silver halide emulsion layer corresponding to unexposed and thus underdeveloped areas forms a soluble silver ion complex with the silver halide solvent present in or activated by the processing composition and migrates to each adjacent nuclei layer. The transferred silver complex is reduced or physically developed in the nuclei layer, thus causing the developing agent to become oxidized. The oxidized developing agent then reacts with the nondiffusible coupler present in each nuclei layer to form imagewise distributions, respectively, of diffusible cyan, magenta and yellow dye as a function of the imagewise exposure of each said silver halide emulsion layer. The diffusible dye can be formed by the reaction of the oxidized developing agent with the nondiffusible coupler or a preformed dye can be released by the reaction of the oxidized developing agent with the nondiffusible coupler, as described above. At least a portion of said imagewise distributions of diffusible cyan, magenta and yellow dyes then diffuse to the image-receiving layer to provide a positive dye image viewable through the transparent support. After being contacted by the alkaline processing composition, a pH-lowering layer in the film unit lowers the pH of the film unit to stabilize it. Since the receiving layer does not have to be stripped away from the negative portion of the film unit, the composite structure can be maintained intact subsequent to processing.

50 In the above-described embodiment, the aromatic primary amino color developing agent is preferably a p-phenylenediamine developing agent which is present in the alkaline processing composition. The physical development nuclei may be any of those well known to those in the art such as colloidal metals, e.g., colloidal silver, gold, platinum, palladium, colloidal metal sulfides, e.g., colloidal silver sulfide, zinc sulfide, etc. Materials which form physical development nuclei may also be used such as reducing agents and labile sulfur compounds. The nuclei layer can also be split into two layers, one on each side of the photosensitive silver halide emulsion layer, if desired. The silver halide solvent employed can be any of those well known to those skilled in the art, such as alkali metal and ammonium thiosulfates and thiocyanates, e.g., sodium thiosulfate, ammonium thiosulfate, ammonium thiocyanate, potassium thiocyanate, etc., and may be incorporated in a separate layer, if desired, either in the photosensitive element or in the opaque process sheet. Spacer layers comprising gelatin are preferably employed between the nuclei layers and the photosensitive silver halide emulsion layers to prevent undesirable mixing of the two layers upon coating. The spacer layers may also contain nuclei and nondiffusible coupler capable of reacting with oxidized color developing agent to form an immobile product in order to increase its efficiency. Other details concerning this type of

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photographic chemistry are found in British Pat. No. 904,364, page 19, lines 1-41.

In the above-described embodiments employing nondiffusible couplers, interlayers are generally employed between the various photosensitive Color-Forming Units to scavenge oxidized developing agent and prevent it from forming an unwanted dye in another Color-Forming Unit. Such interlayers would generally comprise a hydrophilic polymer such as gelatin and an immobilizing coupler, as described above, which is capable of reacting with oxidized aromatic primary amino color developing agent to form an immobile product. Such interlayers may also scavenge other materials such as soluble silver ion complexes or mercaptans in the described systems to prevent such materials from contaminating other Color-Forming Units. A developer scavenging interlayer may also be employed in the above-described embodiments adjacent to the support carrying the photosensitive layers to prevent excess color developing agent from staining the image-receiving layer. Such a layer may comprise for example, a fogged silver halide emulsion, or a spontaneously developable silver halide emulsion, physical development nuclei, and a nondiffusible coupler capable of reacting with oxidized color developing agent to form an immobile product. The developer scavenger interlayer may also contain a water-insoluble reactant capable of forming a water-insoluble salt with mercaptans, etc. The developer scavenger interlayer may also be coated with a polymeric timing layer, e.g., gelatin, if desired, to allow for complete development before the developer scavenger interlayer becomes operative.

As previously mentioned, the aromatic primary amino color developing agent employed in the above-described embodiments is preferably present in the alkaline processing composition in the rupturable pod. The color developing agent can also be incorporated into the negative portion of the film unit as a separate layer, e.g., by employing a Schiff base derivative of an aromatic primary amino color developing agent such as that formed by reacting o-sulfobenzaldehyde and N,N-diethyl-3-methyl-4-aminoaniline. Such incorporated developing agent will be activated by the alkaline processing composition. While the incorporated developing agent can be positioned in any layer of the photosensitive element from which it can be readily made available for development upon activation with alkaline processing composition, it is generally either incorporated in the light-sensitive silver halide emulsion layers or in layers contiguous thereto. As mentioned above, aromatic primary amino color developing agents employed in this invention are preferably p-phenylenediamine developing agents. These developing agents are well known to those skilled in the art and include 4-amino-N,N-diethyl-3-methyl aniline hydrochloride, N,N-diethyl-p-phenylenediamine, 2-amino-5-diethylamino toluene, N-ethyl-β-methane-sulfonamido-ethyl-3-methyl-4-aminoaniline, 4-amino-N-ethyl-3-methyl-N-(β-sulfoethyl)aniline, 4-amino-N-ethyl-3-methoxy-N-(β-sulfoethyl)aniline, 4-amino-N-ethyl-N-(β-hydroxyethyl)aniline, 4-amino-N,N-diethyl-3-hydroxymethyl aniline, 4-amino-N-methyl-N-(β-carboxyethyl)aniline, 4-amino-N,N-bis(β-hydroxyethyl)aniline, 4-amino-N,N-bis(β-hydroxyethyl)-3-methyl aniline, 3-acetamido-4-amino-N,N-bis(β-hydroxyethyl)aniline, 4-amino-N-ethyl-N-(2,3,dihydroxypropyl)-3-methyl aniline sulfate salt, 4-amino-N,N-diethyl-3-(3-hydroxypropoxy)aniline, and the like.

In the drawings, various embodiments of the film unit of the invention are shown with the various elements greatly magnified for purposes of illustration only and wherein like number appearing in the various figures refer to the like components.

In FIG. 1, rupturable containers 11 and 13 are positioned transverse a leading edge of the photosensitive laminate and are held in place by binding means 30, which can be a pressure-sensitive tape, which encloses that edge of the laminate. The other edges of the photosensitive laminate are similarly enclosed with binding means 31, 32 and 33 which enhance the structural integrity of the laminate and prevent leakage of

processing solution during and after photographic processing when rupturable containers 11 and 13 are broken open by pressure-applying members 36 to discharge their contents into the photosensitive laminate.

5 In FIG. 2, film unit 10 comprises a first rupturable container 11 containing, prior to passing between pressure-applying members 36, an alkaline processing composition containing an opacifying agent, rupturable container 13 containing an opacifying composition, and a photosensitive laminate comprising top transparent sheet 29 coated with polymeric acid layer 28 and polymeric timing layer 27 and a photosensitive element comprising transparent support layer 15 coated with an image-receiving layer 16, permeable support 18, cyan dye image-providing layer 19, red-sensitive silver halide emulsion layer 20, barrier interlayer 21, magenta dye image-providing layer 22, green-sensitive silver halide emulsion layer 23, barrier interlayer 24, yellow dye image-providing layer 25 and blue-sensitive silver halide emulsion layer 26. Exposure of the film unit takes place through the top transparent sheet 29 which is preferably an actinic radiation transmissive flexible sheet material.

In FIG. 3, the film unit of FIG. 2 has been passed between pressure-applying members 36 such as would be found in a camera, thus causing rupturable containers 11 and 13 to collapse. The alkaline processing composition containing an opacifying agent is discharged from container 11 between the polymeric timing layer 27 and the blue-sensitive silver halide emulsion layer 26 while the opacifying composition is discharged between the permeable support 18 and the image-receiving layer 16. After development and image transfer has taken place, a positive, right-reading image may be viewed through transparent support 15.

FIG. 4, FIG. 5 and FIG. 6 illustrate other embodiments of the film unit of my invention. The embodiment of FIG. 4 is similar to the embodiment of FIG. 2 with the exception that the alkaline processing composition is contained in the second or lower rupturable container and the photosensitive layer arrangement has been reversed to facilitate exposure from the bottom rather than the top side of the film unit.

The embodiment illustrated in FIG. 5 is similar to the embodiment shown in FIG. 2 with the exception that it contains opaque reflective layer 17 between the permeable support 18 and image-receiving layer 16 and the first or upper rupturable container contains an opacifying composition while the second or lower rupturable container contains the alkaline processing composition. As in FIG. 2, exposure in FIG. 5 takes place from the top side and the transferred positive image is viewed from the bottom side.

FIG. 6 illustrates still another embodiment similar to FIG. 2 with the exception that the top transparent sheet is replaced by opaque layer 36, the first or upper rupturable container does not contain any opacifying agent and the photosensitive layer arrangement has been reversed to facilitate exposure from the bottom rather than the top side of the film unit.

While FIGS. 2-6 indicate that the two rupturable containers are separated from each other, this is done merely for purposes of illustration. Since the layers in the film unit are actually very thin, the two rupturable containers in actual practice are superimposed on each other. If desired, one processing container with two compartments, such as that shown in FIG. 2 of U.S. Pat. No. 3,473,925, may be employed in my invention. In that case, each compartment would serve as a rupturable container and this feature is within the scope of my invention.

Due to the particular chemistry of the image-producing materials described herein, various embodiments of the film unit of my invention can be interchangeably employed in cameras with different optical systems which is not feasible with other types of image-providing materials. For example, if the photosensitive layers in either FIG. 2 or FIG. 4 are replaced by a pan-sensitized silver halide emulsion having a dye image-providing material associated therewith as described previously or having three such dye image-provid-

ing materials associated therewith as described in copending U.S. application Ser. No. 58,195 of Walter M. Bush filed of even date herewith for black-and-white reproduction, the film unit could be exposed from either the top side or the bottom side to provide a transferred positive image. Such a film unit could thus be employed in a camera similar to that illustrated in U.S. Pat. No. 3,447,437 with an image-reversing optical system (exposure from the bottom side) or in a similar camera without the image-reversing optical system (exposure from the top side) to provide a right-reading, positive image in the image-receiving layer which would be viewable through the transparent support.

In a multicolor system, the embodiments illustrated in FIG. 4 and FIG. 6 could be employed in a camera similar to that illustrated in U.S. Pat. No. 3,447,437 with an image-reversing optical system to provide a right-reading, positive image in the image-receiving layer. By modifying the embodiments illustrated in FIG. 4 and FIG. 6 in the manner illustrated in FIG. 2 and FIG. 5 respectively, the same type of chemistry can be employed in film units for use in a camera similar to that illustrated in U.S. Pat. No. 3,447,437 but without an image-reversing optical system to also provide a right-reading, positive image in the image-receiving layer.

In the embodiments of my film unit as illustrated in FIG. 5 and FIG. 6, the opacifying composition in one container is separated from the alkaline processing composition which is present in the other container. These embodiments are particularly useful when it is desired to keep these two components separated from each other, e.g., when the opacifier is present in an unusually high concentration which might interfere with the diffusion of the alkaline processing composition or when the components might react with each other, etc.

The film unit of my invention may be constructed by assembling the various parts in an atmosphere maintained at a pressure lower than atmospheric pressure and by sealing the top sheet and image-receiving element to the photosensitive element along their edges in order to prevent the admission of air between them. The exclusion of air between the various sheets and the photosensitive element is desirable in order to prevent air bubbles from being entrained in the processing composition which would form discontinuities in the positive image. Details of this method of assembly and other methods for assuring a uniform distribution of processing composition between two sheets are described in Belgian Pat. No. 711,897.

The film unit of my invention can also contain a liquid trap at the opposite end in which the processing compositions are introduced in order to trap any excess processing composition and keep it from being expelled from the film unit. The liquid trap may also function to let air escape, if any is present. Such liquid traps are disclosed, for example, in Belgian Pat. No. 711,899.

If it is desired to have residual water in the film unit leave the system after processing, this may be accomplished by incorporating into the film unit a desiccating layer to absorb water or by providing access to the atmosphere in order to let the water evaporate, e.g., by employing a water-permeable top sheet or a water-permeable film support for the image-receiving layer or by allowing water to evaporate through the liquid traps in the film unit as described above, etc.

Rupturable containers 11 and 13 can be of the type disclosed in U.S. Pat. Nos. 2,543,181; 2,634,886; 2,653,732; 2,723,051; 3,056,492; 3,056,491 and 3,152,515. In general such containers comprise a rectangular sheet of fluid and air-impervious material folded longitudinally upon itself to form two walls which are sealed to one another along their longitudinal and end margins to form a cavity in which processing composition is contained. The longitudinal marginal seals are made weaker than the end margin seals so as to become unsealed in response to the hydraulic pressure generated within the fluid contents of the containers by the application of a compressive force to the outside walls of the containers.

As illustrated in FIGS. 1 and 2, containers 11 and 13 are fixedly positioned and extend transverse a leading edge of the

photosensitive laminate so that a compressive force applied to said containers will effect a unidirectional discharge of the container's contents into the film unit. In FIG. 2, the weak longitudinal marginal seals 35 are directed towards the interfaces 5 between layers 27 and 26 and between layers 16 and 18 to facilitate this operation.

In FIG. 3, after containers 11 and 13 have been broken open, they can be detached from the photosensitive laminate along with the upper portion of binding means 30. The end flap of binding means 30 which was previously adhered to container 11 may then be folded up over the end of the laminate to maintain its structural integrity.

In the performance of a multicolor diffusion transfer process employing the film unit of FIG. 2, the unit is exposed 15 to radiation incident on the photosensitive laminate's upper surface through transparent sheet 29. Subsequent to exposure, the film unit 10 is processed by passing it between pressure-applying members 36 in order to apply compressive pressure to frangible containers 11 and 13 and to effect rupture of longitudinal seals 35 and distribution of alkaline processing composition containing an opacifying agent between layers 27 and 26 and distribution of opacifying composition between layers 16 and 18 of the film unit 10. The alkaline processing composition permeates the silver halide emulsion layers 26, 23 and 20 to initiate development of the latent images contained therein. Diffusible yellow, magenta and cyan dye images are formed from material in layers 25, 22 and 19 as a function of the imagewise exposure of their associated emulsions. At least 30 part of the imagewise distributions of mobile yellow, magenta and cyan dyes transfer, by diffusion, to the image-receiving layer 16 to provide a positive dye image therein. This positive, right-reading image can then be viewed through transparent support layer 15 on the opacifying composition background. 35 Since the receiving layer does not have to be stripped away from the negative portion of the film unit, the composite structure can be maintained intact subsequent to said processing.

In a color film unit according to the invention, each silver halide emulsion layer containing a dye image-providing material or having the dye image-providing material present in a contiguous layer may be separated from the other silver halide emulsion layers in the negative portion of the film unit by materials in addition to those described above, including 40 gelatin, calcium alginate, or any of those disclosed in U.S. Pat. No. 3,384,483, polymeric materials such as polyvinylamides as disclosed in U.S. Pat. No. 3,421,892 or any of those disclosed in U.S. Pat. Nos. 2,992,104; 3,043,692; 3,044,873; 3,061,428; 3,069,263; 3,069,264; 3,121,011; and 3,427,158.

Generally speaking, except where noted otherwise, the silver halide emulsion layers in the invention comprise photosensitive silver halide dispersed in gelatin and are about 0.6 to 6 microns in thickness; the dye image-providing materials are dispersed in an aqueous alkaline solution-permeable polymeric binder, such as gelatin, as a separate layer about 1 to 7 microns in thickness; and the alkaline solution-permeable polymeric interlayers, e.g., gelatin, are about 1 to 5 microns in thickness. Of course, these thicknesses are approximate only and can be modified according to the product desired. In addition to gelatin, other suitable hydrophilic materials include 50 both naturally occurring substances such as proteins, cellulose derivatives, polysaccharides such as dextran, gum arabic and the like; and synthetic polymeric substances such as water-soluble polyvinyl compounds like poly(vinylpyrrolidone), acrylamide polymers and the like.

The photographic emulsion layers and other layers of a photographic element employed in the practice of this invention can also contain alone or in combination with hydrophilic, water-permeable colloids, other synthetic polymeric compounds such as dispersed vinyl compounds such as in latex form and particularly those which increase the dimensional stability of the photographic materials. Suitable synthetic polymers include those described, for example, in Nottorf U.S. Pat. No. 3,142,568, issued July 28, 1964; White U.S. Pat. No. 3,193,386, issued July 6, 1965; Houck et al. U.S. Pat. No.

3,062,674, issued Nov. 6, 1962; Houck et al. U.S. Pat. No. 3,220,844, issued Nov. 30, 1965; Ream et al. U.S. Pat. No. 3,287,289, issued Nov. 22, 1966; and Dykstra U.S. Pat. No. 3,411,911, issued Nov. 19, 1968. Particularly effective are water-insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methylacrylate, those which have cross-linking sites which facilitate hardening or curing, and those having recurring sulfobetaine units as described in Dykstra Canadian Pat. No. 774,054.

Any material can be employed as the image-receiving layer in this invention as long as the desired function of mordanting or otherwise fixing the dye images will be obtained. The particular material chosen will, of course, depend upon the dye to be mordanted. If acid dyes are to be mordanted, the image-receiving layer can contain basic polymeric mordants such as polymers of amino guanidine derivatives of vinyl methyl ketone such as described in the Minsk U.S. Pat. No. 2,882,156 granted Apr. 14, 1959. Other mordants useful in our invention include poly-4-vinylpyridine, the 2-vinylpyridine polymer metho-p-toluene sulfonate and similar compounds described in Sprague et al. U.S. Pat. No. 2,484,430 granted Oct. 11, 1949, and cetyl trimethylammonium bromide, etc. Effective mordanting compositions are also described in Whitmore U.S. Pat. No. 3,271,148 and Bush U.S. Pat. No. 3,271,147. The mordanting compositions described in the Whitmore patent comprise at least one hydrophilic organic colloid containing a finely divided, uniform dispersion of droplets or globules of a high-boiling, water-immiscible organic solvent in which is dissolved a high concentration of a cationic, nonpolymeric, organic dye-mordanting compound for acid dyes. The mordanting compositions described in the Bush patent comprise at least one hydrophilic organic colloid containing a finely divided, uniform dispersion of particles of a salt of an organic acidic composition containing free acid moieties and a cationic, nonpolymeric organic dye-mordanting compound for acid dyes. Useful cationic or basic organic dye-mordanting compounds for dyes include quaternary ammonium and phosphonium, and ternary sulfonium compounds in which there is linked to the N, P, or S onium atom at least one hydrophobic ballast group such as long-chain alkyl or substituted alkyl groups. Furthermore, the image-receiving layer can be sufficient by itself to mordant the dye as in the case of use of an alkaline solution-permeable polymeric layer such as N-methoxymethyl polyhexylmethylen adipamide; partially hydrolyzed polyvinyl acetate; polyvinyl alcohol with or without plasticizers; cellulose acetate; gelatin; and other materials of similar nature. Generally, good results are obtained when the image-receiving layer, preferably alkaline solution-permeable, is transparent and about 0.25 to about 0.04 mil in thickness. This thickness, of course, can be modified depending upon the result desired. The image-receiving layer can also contain ultraviolet absorbing materials to protect the mordanted dye images from fading due to ultraviolet light and/or brightening agents such as the stilbenes, coumarins, triazines, oxazoles, etc.

Use of a pH-lowering layer in the film unit of the invention will usually increase the stability of the transferred image. Generally, the pH-lowering layer will effect a reduction in the pH of the image layer from about 13 to 14 or to at least 11 and preferably 5-8 within a short time after imbibition. For example, polymeric acids as disclosed in U.S. Pat. No. 3,362,819 may be employed. Such polymeric acids reduce the pH of the film unit after development to terminate further dye transfer and thus stabilize the dye image. Such polymeric acids comprise polymers containing acid groups, such as carboxylic acid and sulfonic acid groups, which are capable of forming salt with alkali metals, such as sodium or potassium, or with organic bases, particularly quaternary ammonium bases, such as tetramethyl ammonium hydroxide. The polymers can also contain potentially acid-yielding groups such as anhydrides or lactones or other groups which are capable of reacting with bases to capture and retain them. Generally the most useful polymeric acids contain free carboxyl groups, being insoluble

in water in the free acid form and which form water-soluble sodium and/or potassium salts. Examples of such polymeric acids include dibasic acid half-ester derivatives of cellulose which derivatives contain free carboxyl groups, e.g., cellulose acetate hydrogen phthalate, cellulose acetate hydrogen glutarate, cellulose acetate hydrogen succinate, ethyl cellulose hydrogen succinate, ethyl cellulose acetate hydrogen succinate, cellulose acetate succinate hydrogen phthalate; ether and ester derivatives of cellulose modified with sulfoanhydrides, e.g., with ortho-sulfobenzoic anhydride; polystyrene sulfonic acid; carboxymethyl cellulose; polyvinyl hydrogen phthalate; polyvinyl acetate hydrogen phthalate; polyacrylic acid; acetals of polyvinyl alcohol with carboxy or sulfo substituted aldehydes, e.g., O-, M- or p-benzaldehyde sulfonic acid or carboxylic acid; partial esters of ethylene/maleic anhydride copolymers; partial esters of methyl-vinyl ether/maleic anhydride copolymers; etc. In addition, solid monomeric acid materials could also be used such as palmitic acid, oxalic acid, sebacic acid, hydrocinnamic acid, metanilic acid, paratoluenesulfonic acid and benzenedisulfonic acid. Other suitable materials are disclosed in U.S. Pat. No. 3,422,075, and 2,635,048.

The pH-lowering layer is usually about 0.3 to about 1.5 mils in thickness. Although the pH-lowering layer is usually located in the receiver portion of the film unit between the support and the image-receiving layer, it can actually be located anywhere within the film unit as long as the desired function is obtained. For example, a polymeric acid layer could be located in the negative portion of the film unit, as disclosed in U.S. Pat. No. 3,362,821, with the polymeric acid encapsulated in a polymeric material and dispersed in an alkaline solution-permeable binder. In this instance, the processing solution would quickly diffuse through the element to permeate the silver halide emulsion layers. After the processing solution has permeated through the polymeric "shell" surrounding the dispersed particles of polymeric acid, the pH of the film unit would then decrease, thus stabilizing the film unit as a whole. The pH-lowering layer could also be located on the top sheet which is superposed over the photosensitive element of the film unit of the invention. The alkaline processing composition which is discharged from a rupturable container would diffuse upward to contact the pH-lowering layer, become acidic and then diffuse downward into the negative portion of the photosensitive element, thus lowering the pH of the film unit as a whole after development and imagewise diffusion of the various dyes have taken place.

An inert timing or spacer layer coated over the pH-lowering layer can also be used to "time" or control the pH reduction of the film unit as a function of the rate at which the alkali diffuses through the inert spacer layer. Examples of such timing layers include gelatin, polyvinyl alcohol or any of those disclosed in U.S. Pat. No. 3,455,686. The timing layer is also effective in evening out the various reaction rates over a wide range of temperatures, e.g., premature pH reduction is prevented when imbibition is effected at temperatures above room temperature, for example, at 95° to 100° F. The timing layer is usually about 0.1 to about 0.7 mil in thickness. Especially good results are obtained when the timing layer comprises a hydrolyzable polymer or a mixture of such polymers which are slowly hydrolyzed by the processing composition. Examples of such hydrolyzable polymers include polyvinyl acetate, polyamides, polyvinyl ethers, partial acetate of polyvinyl alcohol, etc.

The alkaline processing composition employed in this invention is the conventional aqueous solution of an alkaline material, e.g., sodium hydroxide, sodium carbonate or an amine such as diethylamine, preferably possessing a pH in excess of 12. The solution also preferably contains a viscosity-increasing compound such as a high molecular weight polymer, e.g., a water-soluble ether inert to alkaline solutions such as hydroxyethyl cellulose or alkali metal salts of carboxymethyl cellulose such as sodium carboxymethyl cellulose. A concentration of viscosity-increasing compound of about 1 to about 5

percent by weight of the processing composition is preferred which will impart thereto a viscosity of about 100 c.p.s. to about 200,000 cps. If desired, an adhesive may be added to the processing composition to further increase the adhesion of the various sheets to the photosensitive element after processing.

The alkaline processing composition employed in this invention can also contain an auxiliary or accelerating developing agent such as p-methylaminophenol, 2,4-diaminophenol, p-benzylaminophenol, hydroquinone, tolulydroquinone, phenylhydroquinone, 4-methylphenylhydroquinone, etc. A plurality of auxiliary or accelerating developing agents such as those disclosed in U.S. Pat. No. 3,039,896 can also be employed. Such auxiliary or accelerating developing agents can be employed either in the liquid processing composition or may be contained, at least in part, in any layer or layers of the film unit such as the silver halide emulsion layers, the dye image-providing material layers, interlayers, image-receiving layer, etc.

The alkaline processing composition employed in this invention can also contain a desensitizing agent such as methylene blue, nitro-substituted heterocyclic compounds, 4,4'-bi-pyridinium salts, etc., to insure that the photosensitive element is not further exposed after it is removed from the camera for processing.

While the alkaline processing composition and opacifying composition used in this invention can be employed in rupturable containers, as described previously, to conveniently facilitate the introduction of the compositions, into the film unit, other methods of inserting these compositions into the film unit could also be employed, e.g., interjecting such compositions with communicating members similar to hypodermic syringes which are attached either to a camera or camera cartridge.

Any opacifying agent can be employed in the alkaline processing composition or as a separate opacifying composition in my invention as long as it provides the desired opacity to light. Examples of opacifying agents include carbon black, barium sulfate, zinc oxide, barium stearate, silver flake, silicates, alumina, zirconium oxide, zirconium acetyl acetate, sodium zirconium sulfate, kaolin, mica, titanium dioxide, organic dyes such as the nigratosines, or mixtures thereof in widely varying amounts depending upon the degree of opacity desired. In general, the concentration of opacifying agent should be sufficient to prevent further exposure of the film unit's silver halide emulsion or emulsions by ambient actinic radiation transversing through the film unit subsequent to distribution of the processing composition and various opacifying agents into the film unit. For example, carbon black or titanium dioxide will provide sufficient opacity when they are present in the alkaline processing composition or in a separate opacifying composition in an amount of from about 5 to 40 percent by weight. After the processing solution and various opacifying agents have been distributed into the film unit, processing may take place out of the camera in the presence of actinic radiation in view of the fact that the silver halide emulsion or emulsions of the laminate are surrounded by opaque material. If the illustrated binding tapes are also opaque, edge leakage of actinic radiation incident on the silver halide emulsion or emulsions will also be prevented.

As mentioned above, the opacifying agent can either be employed in the alkaline processing composition or in a separate opacifying composition. When it is employed in a separate opacifying composition, it can be employed by itself but is preferably dispersed in a film-forming binder, e.g., an alkaline solution-permeable polymeric binder such as polyvinyl alcohol, gelatin, etc.

The alkaline solution-permeable, substantially opaque, light-reflective layer 17 of FIG. 5 can generally comprise any opacifier dispersed in a binder as long as it has the desired properties. Particularly desirable are white light-reflective layers since they would be esthetically pleasing backgrounds on which to view a transferred dye image and would also possess

the optical properties desired for reflection of incident radiation. Suitable opacifying agents include titanium dioxide, barium sulfate, zinc oxide, barium stearate, silver flake, silicates, alumina, zirconium oxide, zirconium acetyl acetate, sodium zirconium sulfate, kaolin, mica, or mixtures thereof in widely varying amounts depending upon the degree of opacity desired. The opacifying agents can be dispersed in any binder such as an alkaline solution-permeable polymeric matrix such as, for example, gelatin, polyvinyl alcohol, and the like. Brightening agents such as the stilbenes, coumarins, triazines and oxazoles can also be added to the light-reflective layer, if desired. When it is desired to increase the opacifying capacity of the light-reflective layer, dark-colored opacifying agents may be added to it, e.g., carbon black, nigratosine dyes, etc. Another technique to increase the opacifying capacity of the light-reflective layer is to employ a separate opaque layer underneath it comprising, e.g., carbon black, nigratosine dyes, etc., dispersed in an alkaline solution-permeable polymeric matrix such as, for example, gelatin, polyvinyl alcohol, and the like. Such an opaque layer would generally have a density of at least 4 and preferably greater than 7 and would be substantially opaque to actinic radiation. The opaque layer may also be combined with a developer scavenger layer if one is present. The light-reflective and opaque layers are generally 1 to 6 mils in thickness although they can be varied depending upon the opacifying agent employed, the degree of opacity desired, etc.

The opaque layer 36 of FIG. 6 can comprise any opacifying agent described above dispersed in a binder so long as it has the desired opacity. The opaque layer of FIG. 6 is similar to the opaque layer of FIG. 5 with the exception that the binding agent does not have to be alkaline solution permeable, i.e., it can be any film-forming polymeric material such as polyesters, cellulose esters, polycarbonates, etc.

The transparent sheet in several embodiments of the film assembly of my invention can be any transparent material as long as it does not deleteriously effect the photographic properties of the film unit and is dimensionally stable. Typical actinic radiation transmissive flexible sheet materials include cellulose nitrate film, cellulose acetate film, cellulose acetate butyrate, poly(vinyl acetal) film, polystyrene film, poly(ethyleneterephthalate) film, polycarbonate film, poly- α -olefins such as polyethylene and polypropylene film, and related films or resinous materials as well as glass. The transparent sheet is usually about 2 to 6 mils in thickness. If desired, an adhesive layer activatable by the processing composition may be present on the transparent sheet in order to increase its adhesion to the photosensitive element after processing.

While the invention has been described with reference to layers of silver halide emulsions and dye image-providing materials, dotwise coating, such as would be obtained using a gravure printing technique, could also be employed. In this technique, small dots of blue, green and red-sensitive emulsions have associated therewith, respectively, dots of yellow, magenta and cyan color-providing substances. After development, the transferred dyes would tend to fuse together into a continuous tone.

The photographic layers employed in the practice of this invention can contain surfactants such as saponin, anionic compounds such as the alkyl aryl sulfonates described in Baldsieff U.S. Pat. No. 2,600,831; amphoteric compounds such as those described in Ben-Ezra U.S. Pat. No. 3,133,816; and water soluble adducts of glycidol and an alkyl phenol such as those described in Olin Mathieson British Pat. No. 1,022,878.

The various layers, including the photographic layers, employed in the practice of this invention can contain light-absorbing materials and filter dyes such as those described in Sawday U.S. Pat. No. 3,253,921; Gasper U.S. Pat. No. 2,274,782; Silverstein et al. U.S. Pat. No. 2,527,583 and Van Campen U.S. Pat. No. 2,956,879. If desired, the dyes can be mordanted, for example, as described in Milton et al. U.S. Pat. No. 3,282,699.

The sensitizing dyes and other addenda used in the practice of this invention can be added from water solutions or suitable organic solvent solutions can be used. The compounds can be added using various procedures including those described in Collins et al. U.S. Pat. No. 2,912,343; McCrossen et al. U.S. Pat. No. 3,342,605; Audran U.S. Pat. No. 2,996,287 and Johnson et al. U.S. Pat. No. 3,425,835.

The photographic layers used in the practice of this invention can be coated by various coating procedures including dip coating, air knife coating, curtain coating, or extrusion coating using hoppers of the type described in Beguin U.S. Pat. No. 2,681,294. If desired, two or more layers can be coated simultaneously by the procedures described in Russell U.S. Pat. No. 2,761,791 and Wynn British Pat. No. 837,095. This invention also can be used for silver halide layers coated by vacuum evaporation as described in British Pat. No. 968,453 and Lu Valle et al. U.S. Pat. No. 3,219,451.

The photographic and other hardenable layers used in the practice of this invention can be hardened by various organic or inorganic hardeners, alone or in combination, such as the aldehydes, and blocked aldehydes, ketones, carbocyclic and carbonic acid derivatives, sulfonate esters, sulfonyl halides and vinyl sulfonyl esters, active halogen compounds, epoxy compounds, aziridines, active olefins, isocyanates, carbodiimides, mixed function hardeners and polymeric hardeners such as oxidized polysaccharides like dialdehyde starch and oxyguargum and the like.

The following examples further illustrate the invention:

EXAMPLE 1 (FIG. 2 EMBODIMENT)

A photosensitive element is prepared by coating the following layers in the order recited on an alkaline solution-permeable polyvinyl alcohol film support:

1. Nuclei layer of cyan image transfer coupler 1-hydroxy-4-(3-octadecylcarbamylphenylthio)-N-ethyl-3',5'-dicarboxy-2-naphthanimide (49 mg./ft.²) colloidal palladium (0.24 mg./ft.²) and gelatin (50 mg./ft.²)

2. Spacer layer of gelatin (100 mg./ft.²)

3. Red-sensitive gelatin-silver bromide emulsion (110 mg. gelatin/ft.² and 70 mg. silver/ft.²), 1-hydroxy-N-[α -(2,4-di-tert-aminophenoxy)butyl]-2-naphthamide (87 mg./ft.²) and di-n-butylphthalate (44 mg./ft.²)

4. Spacer layer of gelatin (100 mg./ft.²)

5. Nuclei layer of cyan image transfer coupler 1-hydroxy-4-(3-octadecylcarbamylphenylthio)-N-ethyl-3',5'-dicarboxy-2-naphthanimide (49 mg./ft.²) colloidal palladium (0.24 mg./ft.²) and gelatin (50 mg./ft.²)

6. Barrier Interlayer of 1-hydroxy-N-[α -(2,4-di-tert-aminophenoxy)butyl]-2-naphthamide (87 mg./ft.²), di-n-butylphthalate (44 mg./ft.²), Carey Lea Silver (10 mg./ft.²), colloidal palladium (0.48 mg./ft.²) and gelatin (125 mg./ft.²)

7. Nuclei layer of magenta image transfer coupler 1-phenyl-3-(3,5-disulfonylbenzamido)-4-(6-hydroxy-4-pentadecylphenylazo)-5-pyrazolone, dipotassium salt (38 mg./ft.²), colloidal palladium (0.24 mg./ft.²) and gelatin (50 mg./ft.²)

8. Spacer layer of gelatin (100 mg./ft.²)

9. Green-sensitive gelatin-silver bromide emulsion (110 mg. gelatin/ft.² and 70 mg. silver/ft.²), 1-hydroxy-N-[α -(2,4-di-tert-aminophenoxy)butyl]-2-naphthamide (87 mg./ft.²) and di-n-butylphthalate (44 mg./ft.²)

10. Spacer layer of gelatin (100 mg./ft.²)

11. Nuclei layer of magenta image transfer coupler 1-phenyl-3-(3,5-disulfonylbenzamido)-4-(6-hydroxy-4-pentadecylphenylazo)-5-pyrazolone, dipotassium salt (38 mg./ft.²), colloidal palladium (0.24 mg./ft.²) and gelatin (50 mg./ft.²)

12. Barrier Interlayer of 1-hydroxy-N-[α -(2,4-di-tert-aminophenoxy)butyl]-2-naphthamide (87 mg./ft.²), di-n-butylphthalate (44 mg./ft.²), Carey Lea Silver (10 mg./ft.²), colloidal palladium (0.48 mg./ft.²) and gelatin (125 mg./ft.²)

13. Nuclei layer of yellow image transfer coupler α -Pivalyl- α -(3-octadecylcarbamylphenylthio)-4-sulfoacetanilide potassium salt (60 mg./ft.²), colloidal palladium (0.24 mg./ft.²) and gelatin (50 mg./ft.²)

14. Spacer layer of gelatin (100 mg./ft.²)

15. Blue-sensitive gelatin-silver bromide emulsion (110 mg. gelatin/ft.² and 70 mg. silver/ft.²), 1-hydroxy-N-[α -(2,4-di-tert-aminophenoxy)butyl]-2-naphthamide (87 mg./ft.²) and di-n-butylphthalate (44 mg./ft.²)

16. Spacer layer of gelatin (100 mg./ft.²)

17. Nuclei layer of yellow image transfer coupler α -Pivalyl- α -(3-octadecylcarbamylphenylthio)-4-sulfoacetanilide potassium salt (60 mg./ft.²), colloidal palladium (0.24 mg./ft.²) and gelatin (50 mg./ft.²)

18. The photosensitive emulsions listed above are negative-type, developing out emulsions. Next, an image-receiving layer of methyl-tri-n-dodecyl-ammonium p-toluenesulfonate (22.5 mg./ft.²), N-n-hexadecyl-N-morpholinium ethosulfate (150 mg./ft.²) and gelatin (743 mg./ft.²) is coated on a transparent cellulose acetate film support. The following processing composition is employed in the first processing pod:

20	Water	100 ml.
	Piperidino hexose reductone	0.08 g.
	Sodium hydroxide	3.0 g.
	3-methoxy-4-amino-N-ethyl-N- β -hydroxyethylaniline	3.0 g.
	Hydroxyethylcellulose	3.2 g.
	Carbon black	0.6 g.

The following processing composition is employed in the second processing pod:

30	Water	100 ml.
	Hydroxyethylcellulose	3.2 g.
	Titanium dioxide	6.0 g.

A transparent sheet of cellulose acetate film base is then superposed over the top layer 17 of the element with the first processing pod placed in between the film base and the element. Next, the second processing pod and the image-receiving layer are positioned on the other side of the photosensitive element with the pod in between the image-receiving layer and the photosensitive element. The element is then exposed through the transparent sheet to a graduated-density multicolor test object. The processing compositions are spread from the pods into the film unit by passing the transfer "sandwich" between a pair of juxtaposed pressure rollers. After about 3 minutes at 20° C., a multicolor reproduction of the test object is observed on a white background when viewed through the transparent film support side of the unit.

EXAMPLE 2 (FIG. 4 EMBODIMENT)

A photosensitive element is prepared by coating the following layers in the order recited on an alkaline solution-permeable polyvinyl alcohol film support:

1. Blue-sensitive gelatin-silver bromide emulsion (110 mg. gelatin/ft.² and 70 mg. silver/ft.²), 1-hydroxy-N-[α -(2,4-di-tert-aminophenoxy)butyl]-2-naphthamide (87 mg./ft.²) and di-n-butylphthalate (44 mg./ft.²)

2. Spacer layer of 1-hydroxy-N-[α -(2,4-di-tert-aminophenoxy)butyl]-2-naphthamide (20 mg./ft.²), gelatin (100 mg./ft.²) and di-n-butylphthalate (10 mg./ft.²)

3. Nuclei layer of yellow image transfer coupler α -Pivalyl- α -(3-octadecylcarbamylphenylthio)-4-sulfoacetanilide potassium salt (120 mg./ft.²), colloidal palladium (0.48 mg./ft.²) and gelatin (100 mg./ft.²)

4. Barrier Interlayer of 1-hydroxy-N-[α -(2,4-di-tert-aminophenoxy)butyl]-2-naphthamide (87 mg./ft.²), di-n-butylphthalate (44 mg./ft.²), Carey Lea Silver (10 mg./ft.²), colloidal palladium (0.48 mg./ft.²) and gelatin (125 mg./ft.²)

5. Green-sensitive gelatin-silver bromide emulsion (110 mg. gelatin/ft.² and 70 mg. silver/ft.²), 1-hydroxy-N-[α -(2,4-di-tert-aminophenoxy)butyl]-2-naphthamide (87 mg./ft.²) and di-n-butylphthalate (44 mg./ft.²)

6. Spacer layer of 1-hydroxy-N-[α -(2,4-di-tert-aminophenoxy)butyl]-2-naphthamide (20 mg./ft.²), gelatin (100 mg./ft.²) and di-n-butylphthalate (10 mg./ft.²)

7. Nuclei layer of magenta image transfer coupler 1-phenyl-3-(3,5-disulfonylbenzamido)-4-(6-hydroxy-4-pentadecylphenylazo)-5-pyrazolone, dipotassium salt (75 mg./ft.²), colloidal palladium (0.48 mg./ft.²) and gelatin (100 mg./ft.²)

8. Spacer layer of gelatin (100 mg./ft.²)

8. Barrier interlayer of 1-hydroxy-N-[α -(2,4-di-tert-
amylphenoxy)butyl]-2-naphthamide (87 mg./ft.²), di-n-butylphthalate (44 mg./ft.²), Carey Lea Silver (10 mg./ft.²), colloidal palladium (0.48 mg./ft.²) and gelatin (125 mg./ft.²)

9. Red-sensitive gelatin-silver bromide emulsion (110 mg. gelatin/ft.² and 70 mg. silver/ft.²), 1-hydroxy-N-[α -(2,4-di-tert-
amylphenoxy)butyl]-2-naphthamide (87 mg./ft.²) and di-n-butylphthalate (44 mg./ft.²)

10. Spacer layer of 1-hydroxy-N-[α -(2,4-di-tert-
amylphenoxy)butyl]-2-naphthamide (20 mg./ft.²), gelatin (100 mg./ft.²) and di-n-butylphthalate (10 mg./ft.²)

11. Nuclei layer of cyan image transfer coupler 1-hydroxy-4-(3-octadecylcarbamylphenylthio-N-ethyl-3',5'-dicarboxy-
2-naphthaniilide (97 mg./ft.²), colloidal palladium (0.48 mg./ft.²) and gelatin (100 mg./ft.²)

The photosensitive emulsions listed above are negative-type, developing-out emulsions. An image-receiving layer similar to that of example 1 is coated on a transparent cellulose acetate film support. First and second processing pods are prepared containing the processing compositions listed in example 1. A transparent sheet of cellulose acetate film base is then superposed over the top layer 11 of the element with the second processing pod, i.e., the one containing water, hydroxyethylcellulose and titanium dioxide, placed in between the film base and the element. Next, the first processing pod and the image-receiving layer are positioned on the other side of the photosensitive element with the pod in between the image-receiving layer and the photosensitive element. The element is then exposed through the image-receiving layer to a graduated-density multicolor test object. The film unit is then processed as in example 1 to obtain a multicolor reproduction of the test object on a white background when viewed through the transparent film support side of the unit.

EXAMPLE 3 (FIG. 5 EMBODIMENT)

A photosensitive element is prepared by coating the following layers in the order recited on an alkaline solution-permeable polyvinyl alcohol film support:

1. Spontaneously developable emulsion layer of ZnS nuclei (0.00043 mg./ft.²), silver thiocyanate (30 mg./ft.²), cyan image transfer coupler 1-hydroxy-4-(3-n-octadecylcarbamylphenylthio)-2-(3',5'-dicarboxy)-N-ethylnaphthaniilide (100 mg./ft.²), antistain agent 2-(β -octadecyl)-5-(β -sulfo-tert-butyl)-hydroquinone (potassium salt) (16 mg./ft.²) and gelatin (100 mg./ft.²)

2. Red-sensitive gelatin-silver bromide emulsion (100 mg. gelatin/ft.² and 150 mg. silver/ft.²) and developer inhibitor releasing coupler 1-hydroxy-4-(1-phenyl-5-tetrazolylthio)-2-(2'-n-tetradecyloxy)naphthaniilide (60 mg./ft.²)

3. Barrier layer of gelatin-silver iodide emulsion (100 mg. gelatin/ft.² and 50 mg. silver/ft.²) and antistain agent 2- β -octadecyl)-5-(β -sulfo-tert-butyl)-hydroquinone (potassium salt) (32 mg./ft.²)

4. Spontaneously developable emulsion layer of ZnS nuclei (0.00043 mg./ft.²), silver thiocyanate (20 mg./ft.²), magenta image transfer coupler 1-(4-sulfophenyl)-3-(4-sulfoanilino)-4-(2-hydroxy-4-pentadecylphenylazo)-5-pyrazolonedipotassium salt (50 mg./ft.²), antistain agent 2-(β -octadecyl)-5-(β -sulfo-tert-butyl)-hydroquinone (potassium salt) (16 mg./ft.²) and gelatin (100 mg./ft.²)

5. Green-sensitive gelatin-silver bromide emulsion (100 mg. gelatin/ft.² and 75 mg. silver/ft.²) and developer inhibitor releasing coupler 1-hydroxy-4-(1-phenyl-5-tetrazolylthio)-2-(2'-n-tetradecyloxy)naphthaniilide (60 mg./ft.²)

6. Barrier and yellow filter layer of gelatin silver iodide emulsion (100 mg. gelatin/ft.² and 50 mg. silver/ft.²), antistain agent 2-(β -octadecyl)-5-(β -sulfo-tert-butyl)-hydroquinone (potassium salt) (32 mg./ft.²) and yellow dye 4-(p-methoxyphenylazo)-1(2,4,6-trichlorophenyl)-3-[3-{ α -(2,4-di-tert-
amylphenoxy)acetamido}benzamido]-5-pyrazolone (50 mg./ft.²)

7. Spontaneously developable emulsion layer of ZnS nuclei (0.00043 mg./ft.²), silver thiocyanate (45 mg./ft.²), yellow image transfer coupler α -benzoyl- α -(3-octadecylcarbamylphenylthio)-3,5-dicarboxyacetanilide (150 mg./ft.²),

antistain agent 2-(β -octadecyl)-5-(β -sulfo-tert-butyl)-hydroquinone (potassium salt) (16 mg./ft.²) and gelatin (100 mg./ft.²)

8. Blue-sensitive gelatin-silver bromide emulsion (100 mg. gelatin/ft.² and 75 mg. silver/ft.²) and developer inhibitor releasing coupler 1-hydroxy-4-(1-phenyl-5-tetrazolylthio)-2-(2'-n-tetradecyloxy)naphthaniilide (60 mg./ft.²)

The photosensitive emulsions listed above are negative-type developing-out emulsions. Next, a transparent cellulose acetate film support is coated with

1. an image-receiving layer of methyl-tri-n-dodecyl-ammonium p-toluenesulfonate (22.5 mg./ft.²), N-n-hexadecyl-N-morpholinium ethosulfate (150 mg./ft.²) and gelatin (763 mg./ft.²)

2. Light reflective layer of TiO₂ (2700 mg./ft.²) and gelatin (270 mg./ft.²) and

3. Opaque layer of gelatin (360 mg./ft.²) and carbon black (300 mg./ft.²)

20 The following processing composition is employed in the first processing pod.

25	Water	100 ml.
	Hydroxyethylcellulose	3.2 g.
	Carbon black	6.0 g.

The following processing composition is employed in the second processing pod:

30	Water	100 ml.
	Piperidino hexose reductone	0.08 g.
	Sodium hydroxide	3.0 g.
	3-methoxy-4-amino-N-ethyl-N- β -hydroxyethylaniline	3.0 g.
	Hydroxyethylcellulose	3.2 g.
	Sodium thiosulfate	0.6 g.

A transparent sheet of cellulose acetate film base is then superposed over the top layer 8 of the element with the first processing pod placed between the film base and the element.

40 Next, the second processing pod and the image-receiving element as positioned on the other side of the photosensitive element with the pod in between the image-receiving element and the photosensitive element. The element is then exposed through the transparent sheet to a graduated-density multicolor test object. The processing compositions are spread from the pods into the film unit by passing the transfer "sandwich" between a pair of juxtaposed pressure rollers. After about three minutes at 20° C., a multicolor reproduction of

45 50 the test object is observed on a white background when viewed through the transparent film support side of the unit.

EXAMPLE 4 (FIG. 6 EMBODIMENT)

A photosensitive element is prepared by coating the following layers in the order recited on an alkaline solution-permeable polyvinyl alcohol film support:

1. Blue-sensitive gelatin-silver chlorobromide emulsion (100 mg. gelatin/ft.² and 100 mg. silver/ft.²), yellow image transfer coupler α -pivalyl- α -(4-(N-methyl-N-n-octadecylsulfamyl)phenoxyl)-4-sulfoacetanilide potassium salt (120 mg./ft.²) and fogging agent formyl-4-methylphenylhydrazide (0.5 g./mole of silver chlorobromide)

60 2. Scavenger and yellow filter layer of 1-hydroxy-N-[α -(2,4-di-tert-
amylphenoxy)butyl]-2-naphthamide (45 mg./ft.²), tricresyl phosphate (22 mg./ft.²), Carey Lea Silver (10 mg./ft.²) and gelatin (65 mg./ft.²)

65 3. Green-sensitive gelatin-silver chlorobromide emulsion (90 mg. gelatin/ft.² and 100 mg. silver/ft.²), magenta image transfer coupler 1-phenyl-3-(3,5-disulfobenzamido)-4-(6-hydroxy-4-pentadecylphenylazo)-5-pyrazolone, dipotassium salt (75 mg./ft.²) and fogging agent formyl-4-methylphenylhydrazide (0.5 g./mole of silver chlorobromide)

70 4. Scavenger interlayer of 1-hydroxy-N-[α -(2,4-di-tert-
amylphenoxy)butyl]-2-naphthamide (45 mg./ft.²), tricresyl phosphate (22 mg./ft.²) and gelatin (65 mg./ft.²)

5. Red-sensitive gelatin-silver chlorobromide emulsion (120 mg. gelatin/ft.² and 100 mg. silver/ft.²), cyan image transfer coupler 1-hydroxy-4-{4-[α -(3-pentadecylphenoxy)-butyramido]phenoxy}-N-ethyl-3',5'-dicarboxy-2-naphthalide (75 mg./ft.²) and fogging agent formyl-4-methylphenylhydrazide (0.5 g./mole of silver chlorobromide)

The photosensitive emulsions listed above are internal image emulsions having high internal sensitive and lower surface sensitivity and are prepared by the procedure described in Davey et al. U.S. Pat. No. 2,592,250, issued Apr. 8, 1952. An image-receiving layer similar to that of example 1 is coated on a transparent cellulose acetate film support. The following processing composition is employed in the first processing pod:

Water	100 ml.
Benzyl alcohol	0.5 ml.
Piperidino hexose reductone	0.025 g.
5-Nitrobenzimidazole	0.0005 g.
Sodium hydroxide	1.25 g.
4-Amino-N-ethyl-N- β -hydroxyethylaniline	1.5 g.
Hydroxyethylcellulose	2.5 g.

The following processing composition is employed in the second processing pod:

Water	100 ml.
Hydroxyethylcellulose	3.2 g.
Titanium dioxide	6.0 g.

An opaque sheet of poly(ethyleneterephthalate) is then coated with a pH-lowering layer of polyacrylic acid and timing layer of polyvinyl acetate. The coated opaque sheet is then superposed over the top layer 5 of the element with the first processing pod placed between the coated opaque sheet and the element. Next, the second processing pod and the image-receiving layer are positioned on the other side of the photosensitive element with the pod in between the image-receiving layer and the photosensitive element. The element is then exposed through the image-receiving layer to a graduated-density multicolor test object. The film unit is then processed as in example 3 to obtain a multicolor reproduction of the test object on a white background when viewed through the transparent film support side of the unit.

The invention has been described in detail with particular reference to preferred embodiments thereof, but, it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

I claim:

1. A photographic film unit which is adapted to be processed by passing said unit between a pair of juxtaposed pressure-applying members comprising:
 - a transparent support coated with an image-receiving layer having thereon a photosensitive element comprising at least one photosensitive silver halide emulsion layer, each said silver halide emulsion layer having associated therewith a nondiffusible dye image-providing material capable of reacting with oxidized developing agent to produce a diffusible dye;
 - a top sheet superposed over the outermost layer of said photosensitive element from said transparent support;
 - a first rupturable container being so positioned during processing that a compressive force applied to said first container by said pressure-applying members will effect a discharge of said first container's contents between said top sheet and said outermost layer of said photosensitive element; and
 - a second rupturable container being so positioned during processing that a compressive force applied to said second container by said pressure-applying members will effect a discharge of said second container's contents between said image-receiving layer and the innermost layer of said photosensitive element from said transparent support; said film unit containing a developing agent; one

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of said rupturable containers containing an opacifying agent, and the other said rupturable container containing an alkaline processing composition.

2. The photographic film unit of claim 1 wherein said rupturable containers are positioned transverse at least a portion of a leading edge of said photosensitive element.
3. The photographic film unit of claim 2 wherein said developing agent is an aromatic primary amino color developing agent and the photosensitive portion of said photosensitive element comprises a red-sensitive silver halide emulsion layer having associated therewith a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible cyan dye, a green-sensitive silver halide emulsion layer having associated therewith a non-diffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible magenta dye and a blue-sensitive silver halide emulsion layer having associated therewith a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible yellow dye.
4. The photographic film unit of claim 3 wherein said top sheet is transparent, said first rupturable container contains an alkaline processing composition having therein an opacifying agent and said second rupturable container contains an opacifying agent.
5. The photographic film unit of claim 3 wherein said top sheet is transparent, said first rupturable container contains an opacifying agent and said second rupturable container contains an alkaline processing composition having therein an opacifying agent.
6. The photographic film unit of claim 3 wherein said top sheet is transparent, said first rupturable container contains an opacifying agent, said second rupturable container contains an alkaline processing composition, and said film unit contains an opaque reflecting layer intermediate said image-receiving layer and said photosensitive element.
7. The photographic film unit of claim 3 wherein said top sheet is opaque, said first rupturable container contains an alkaline processing composition and said second rupturable container contains an opacifying agent.
8. The photographic film unit of claim 3 including a pH-lowering layer which is capable of lowering the pH of the film unit subsequent to diffusion therethrough by said alkaline processing composition.
9. The photographic film unit of claim 3 wherein each said nondiffusible coupler is contained in a layer contiguous to each said silver halide emulsion layer.
10. A photographic film unit which is adapted to be processed by passing said unit between a pair of juxtaposed pressure-applying members comprising:
 1. a transparent support coated with an image-receiving layer having thereon a photosensitive element comprising an alkaline solution-permeable support having thereon the following layers in the order recited:
 - a direct positive, red-sensitive silver halide emulsion layer containing a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible cyan dye;
 - an alkaline solution-permeable interlayer containing a compound capable of scavenging oxidized aromatic primary amino color developing agent;
 - a direct positive, green-sensitive silver halide emulsion layer containing a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible magenta dye;
 - an alkaline solution-permeable interlayer containing a compound capable of scavenging oxidized aromatic primary amino color developing agent; and
 - a direct positive, blue-sensitive silver halide emulsion layer containing a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible yellow dye;
 - each said nondiffusible coupler having the formula:

DYE-LINK-(COUP-BALL)_n

or

BALL-LINK-(COUP-SOL)_n

wherein:

1. DYE is a dye radical exhibiting selective absorption in the visible spectrum and containing an acidic solubilizing group;
2. LINK is a connecting radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, an alkylidene radical, a thio radical, a dithio radical and an azoxy radical; 10
3. COUP is a coupler radical selected from the group consisting of a 5-pyrazolone coupler radical, a pyrazolotriazole coupler radical, a phenolic coupler radical and an open-chain ketomethylene coupler radical, said COUP being substituted in the coupling position with said LINK; 15
4. BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render said coupler nondiffusible during development in said alkaline processing composition; 20
5. SOL is selected from the group consisting of a hydrogen atom and an acidic solubilizing group when said color developing agent contains an acidic solubilizing group, and SOL is an acidic solubilizing group when said color developing agent is free of an acidic solubilizing group; and 25
6. n is an integer of 1 to 2 when said LINK is an alkylidene radical, and n is 1 when said LINK is a radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, a thio radical, a dithio radical, and an azoxy radical; 30
- II. a transparent sheet superposed over said blue-sensitive silver halide emulsion layer of said photosensitive element; 35
- III. a first rupturable container being positioned transverse at least a portion of a leading edge of said photosensitive element so that a compressive force applied to said first container by said pressure-applying members will effect a discharge of said first container's contents between said transparent sheet and said underlying blue-sensitive silver halide emulsion layer of said photosensitive element adjacent thereto; and 40
- IV. a second rupturable container being positioned transverse at least a portion of a leading edge of said photosensitive element so that a compressive force applied to said second container by said pressure-applying members will effect a discharge of said second container's contents between said alkaline solution-permeable support of said photosensitive element and said image-receiving layer; 45

said film unit containing an aromatic primary amino color developing agent; one of said rupturable containers containing an opacifying agent and the other said rupturable container containing an alkaline processing composition. 55

11. The photographic film unit of claim 10 wherein said aromatic primary amino color developing agent is a p-phenylenediamine developing agent which is present in said alkaline processing composition, said transparent sheet is 60 coated with, successively, a pH-lowering layer and an alkaline solution-permeable polymeric timing layer on the side thereof which is closest to said photosensitive element, said pH-lowering layer being capable of lowering the pH of the film unit subsequent to diffusion therethrough by said alkaline processing 65 composition, and each said direct positive silver halide emulsion is an internal image emulsion wherein the silver halide forms latent images predominantly inside the silver halide grains.
12. The photographic film unit of claim 11 wherein said first rupturable container contains an alkaline processing composition having therein an opacifying agent and said second rupturable container contains an opacifying agent. 70
13. The photographic film unit of claim 11 wherein said first rupturable container contains an opacifying agent, said 75

second rupturable container contains an alkaline processing composition and said film unit contains an opaque reflecting layer intermediate said image-receiving layer and said photosensitive element.

5. 14. A photographic film unit which is adapted to be processed by passing said unit between a pair of juxtaposed pressure-applying members comprising:
 - I. a transparent support coated with an image-receiving layer having thereon a photosensitive element comprising an alkaline solution-permeable support having thereon the following layers in the order recited:
 - a. a direct positive, blue-sensitive silver halide emulsion layer containing a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible yellow dye;
 - b. an alkaline solution-permeable interlayer containing a compound capable of scavenging oxidized aromatic primary amino color developing agent;
 - c. a direct positive, green-sensitive silver halide emulsion layer containing a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible magenta dye;
 - d. an alkaline solution-permeable interlayer containing a compound capable of scavenging oxidized aromatic primary amino color developing agent; and
 - e. a direct positive, red-sensitive silver halide emulsion layer containing a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible cyan dye;
 - each said nondiffusible coupler having the formula:

DYE-LINK-(COUP-BALL)_n

or

BALL-LINK-(COUP-SOL)_n

wherein:

1. DYE is a dye radical exhibiting selective absorption in the visible spectrum and containing an acidic solubilizing group;
2. LINK is a connecting radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, an alkylidene radical, a thio radical, a dithio radical and an azoxy radical;
3. COUP is a coupler radical selected from the group consisting of a 5-pyrazolone coupler radical, a pyrazolotriazole coupler radical, a phenolic coupler radical and an open-chain ketomethylene coupler radical, said COUP being substituted in the coupling position with said LINK;
4. BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render said coupler nondiffusible during development in said alkaline processing composition;
5. SOL is selected from the group consisting of a hydrogen atom and an acidic solubilizing group when said color developing agent contains an acidic solubilizing group, and SOL is an acidic solubilizing group when said color developing agent is free of an acidic solubilizing group; and
6. n is an integer of 1 to 2 when said LINK is an alkylidene radical, and n is 1 when said LINK is a radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, a thio radical, a dithio radical and an azoxy radical;
- II. a top sheet superposed over said red-sensitive silver halide emulsion layer of said photosensitive element;
- III. a first rupturable container being positioned transverse at least a portion of a leading edge of said photosensitive element so that a compressive force applied to said first container by said pressure-applying members will effect a discharge of said first container's contents between said top sheet and said underlying red-sensitive silver halide

emulsion layer of said photosensitive element adjacent thereto; and

IV. a second rupturable container being positioned transverse at least a portion of a leading edge of said photosensitive element so that a compressive force applied to said second container by said pressure-applying members will effect a discharge of said second container's contents between said alkaline solution-permeable support of said photosensitive element and said image-receiving layer; 5 said film unit containing an aromatic primary amino color developing agent; one of said rupturable containers containing an opacifying agent and the other said rupturable container containing an alkaline processing composition. 10

15. The photographic film unit of claim 14 wherein said aromatic primary amino color developing agent is a p-phenylenediamine developing agent which is present in said alkaline processing composition, said top sheet is coated with, successively, a pH-lowering layer and an alkaline solution-permeable polymeric timing layer on the side thereof which is closest to said photosensitive element, said pH-lowering layer being capable of lowering the pH of the film unit subsequent to diffusion therethrough by said alkaline processing composition, and each said direct positive silver halide emulsion is an internal image emulsion wherein the silver halide forms latent 20 images predominantly inside the silver halide grains. 25

16. The photographic film unit of claim 15 wherein said top sheet is transparent, said first rupturable container contains an opacifying agent and said second rupturable container contains an alkaline processing composition having therein an opacifying agent. 30

17. The photographic film unit of claim 15 wherein said top sheet is opaque, said first rupturable container contains an alkaline processing composition and said second rupturable container contains an opacifying agent. 35

18. A photographic film unit which is adapted to be processed by passing said unit between a pair of juxtaposed pressure-applying members comprising:

I. a transparent support coated with an image-receiving layer having thereon a photosensitive element comprising 40 an alkaline solution-permeable support having thereon the following layers in the order recited:

a. a Color-Forming Unit comprising:

1. a developable emulsion layer of a hydrophilic colloid 45 and a water-insoluble metal salt which is developable by an aromatic primary amino color developing agent to substantial density without exposure to light, said metal salt having contiguous thereto a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible cyan dye; and

2. a red-sensitive silver halide emulsion layer, the silver halide of which has contiguous thereto a nondiffusible development inhibitor-releasing coupler which is capable of reacting with oxidized aromatic primary amino color developing agent to release a diffusible mercaptan development inhibitor which is capable of diffusing imagewise to said adjacent developable emulsion layer to inhibit development therein; 55

b. an alkaline solution-permeable barrier layer comprising a hydrophilic colloid containing a water-insoluble reactant capable of forming a water-insoluble salt with mercaptans; 60

c. a Color-Forming Unit comprising:

1. a developable emulsion layer of a hydrophilic colloid 65 and a water-insoluble metal salt which is developable by an aromatic primary amino color developing agent to substantial density without exposure to light, said metal salt having contiguous thereto a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible magenta dye; and

2. a green-sensitive silver halide emulsion layer the silver halide of which has contiguous thereto a non- 70

diffusible development inhibitor-releasing coupler which is capable of reacting with oxidized aromatic primary amino color developing agent to release a diffusible mercaptan development inhibitor which is capable of diffusing imagewise to said adjacent developable emulsion layer to inhibit development therein;

d. an alkaline solution-permeable barrier layer comprising a hydrophilic colloid containing a water-insoluble reactant capable of forming a water-insoluble salt with mercaptans;

e. a Color-Forming Unit comprising:

1. a developable emulsion layer of a hydrophilic colloid and a water-insoluble metal salt which is developable by an aromatic primary amino color developing agent to substantial density without exposure to light, said metal salt having contiguous thereto a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible yellow dye; and

2. a blue-sensitive silver halide emulsion layer the silver halide of which has contiguous thereto a nondiffusible development inhibitor-releasing coupler which is capable of reacting with oxidized aromatic primary amino color developing agent to release a diffusible mercaptan development inhibitor which is capable of diffusing imagewise to said adjacent developable emulsion layer to inhibit development therein; each said nondiffusible coupler having the formula:

DYE—LINK—(COUP—BALL)_n

or

BALL—LINK—(COUP—SOL)_n

wherein:

1. DYE is a dye radical exhibiting selective absorption in the visible spectrum and containing an acidic solubilizing group;

2. LINK is a connecting radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, an alkylidene radical, a thio radical, a dithio radical and an azoxy radical;

3. COUP is a coupler radical selected from the group consisting of a 5-pyrazolone coupler radical, a pyrazolotriazole coupler radical, a phenolic coupler radical and an open-chain ketomethylene coupler radical, said COUP being substituted in the coupling position with said LINK;

4. BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render said coupler nondiffusible during development in said alkaline processing composition;

5. SOL is selected from the group consisting of a hydrogen atom and an acidic solubilizing group when said color developing agent contains an acidic solubilizing group, and SOL is an acidic solubilizing group when said color developing agent is free of an acidic solubilizing group; and

6. n is an integer of 1 to 2 when said LINK is an alkylidene radical, and n is 1 when said LINK is a radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, a thio radical, a dithio radical and an azoxy radical;

II. a transparent sheet superposed over said blue-sensitive silver halide emulsion layer of said photosensitive element;

III. a first rupturable container being positioned transverse at least a portion of a leading edge of said photosensitive element so that a compressive force applied to said first container by said pressure-applying members will effect a discharge of said first container's contents between said transparent sheet and said underlying blue-sensitive silver

halide emulsion layer of said photosensitive element adjacent thereto; and

IV. a second rupturable container being positioned transverse at least a portion of a leading edge of said photosensitive element so that a compressive force applied to said second container by said pressure-applying members will effect a discharge of said second container's contents between said alkaline solution-permeable support of said photosensitive element and said image-receiving layer; 10
said film unit containing an aromatic primary amino color developing agent; one of said rupturable containers containing an opacifying agent and the other said rupturable container containing an alkaline processing composition.

19. The photographic film unit of claim 18 wherein said aromatic primary amino color developing agent is a p-phenylenediamine developing agent which is present in said alkaline processing composition, said developable emulsion is an emulsion of a hydrophilic colloid, silver thiocyanate and physical development nuclei that can be developed to substantial density without exposure to light, and said transparent sheet is coated with, successively, a pH-lowering layer and an alkaline solution-permeable polymeric timing on the side thereof which is closest to said photosensitive element, said pH-lowering layer being capable of lowering the pH of the film 25 unit subsequent to diffusion therethrough by said alkaline processing composition.

20. The photographic film unit of claim 19 wherein said first rupturable container contains an alkaline processing composition having therein an opacifying agent and said second rupturable container contains an opacifying agent. 30

21. The photographic film unit of claim 19 wherein said first rupturable container contains an opacifying agent, said second rupturable container contains an alkaline processing composition and said film unit contains an opaque reflecting layer intermediate said image-receiving layer and said photosensitive element. 35

22. A photographic film unit which is adapted to be processed by passing said unit between a pair of juxtaposed pressure-applying members comprising: 40

I. a transparent support coated with an image-receiving layer having thereon a photosensitive element comprising an alkaline solution-permeable support having thereon the following layers in the order recited: 45

a. a Color-Forming Unit comprising:

1. a blue-sensitive silver halide emulsion layer, the silver halide of which has contiguous thereto a non-diffusible development inhibitor-releasing coupler which is capable of reacting with oxidized aromatic primary amino color developing agent to release a diffusible mercaptan development inhibitor which is capable of diffusing imagewise to said adjacent developable emulsion layer to inhibit development therein; and 50

2. a developable emulsion layer of a hydrophilic colloid and a water-insoluble metal salt which is developable by an aromatic primary amino color developing agent to substantial density without exposure to light, said metal salt having contiguous thereto a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible yellow dye; 60

b. an alkaline solution-permeable barrier layer comprising a hydrophilic colloid containing a water-insoluble reactant capable of forming a water-insoluble salt with mercaptans; 65

c. a Color-Forming Unit comprising:

1. A green-sensitive silver halide emulsion layer, the silver halide of which has contiguous thereto a non-diffusible development inhibitor-releasing coupler which is capable of reacting with oxidized aromatic primary amino color developing agent to release a diffusible mercaptan development inhibitor which is capable of diffusing imagewise to said adjacent 75

developable emulsion layer to inhibit development therein; and

2. a developable emulsion layer of a hydrophilic colloid and a water-insoluble metal salt which is developable by an aromatic primary amino color developing agent to substantial density without exposure to light, said metal salt having contiguous thereto a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible magenta dye;

d. an alkaline solution-permeable barrier layer comprising a hydrophilic colloid containing a water-insoluble reactant capable of forming a water-insoluble salt with mercaptans;

e. a Color-Forming Unit comprising:

1. a red-sensitive silver halide emulsion layer the silver halide of which has contiguous thereto a nondiffusible development inhibitor-releasing coupler which is capable of reacting with oxidized aromatic primary amino color developing agent to release a diffusible mercaptan development inhibitor which is capable of diffusing imagewise to said adjacent developable emulsion layer to inhibit development therein; and

2. a developable emulsion layer of a hydrophilic colloid and a water-insoluble metal salt which is developable by an aromatic primary amino color developing agent to substantial density without exposure to light, said metal salt having contiguous thereto a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible cyan dye; each said nondiffusible coupler having the formula:

DYE-LINK-(COUP-BALL)_n

or

BALL-LINK-(COUP-SOL)_n

wherein:

1. DYE is a dye radical exhibiting selective absorption in the visible spectrum and containing an acidic solubilizing group;

2. LINK is a connecting radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, an alkylidene radical, a thio radical, a dithio radical and an azoxy radical;

3. COUP is a coupler radical selected from the group consisting of a 5-pyrazolone coupler radical, a pyrazolotriazole coupler radical, a phenolic coupler radical and an open-chain ketomethylene coupler radical, said COUP being substituted in the coupling position with said LINK;

4. BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render said coupler nondiffusible during development in said alkaline processing composition;

5. SOL is selected from the group consisting of a hydrogen atom and an acidic solubilizing group when said color developing agent contains an acidic solubilizing group, and SOL is an acidic solubilizing group when said color developing agent is free of an acidic solubilizing group; and

6. n is an integer of 1 to 2 when said LINK is an alkylidene radical, and n is 1 when said LINK is a radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, a thio radical, a dithio radical and an azoxy radical;

II. a top sheet superposed over the outermost layer of said photosensitive element;

III. a first rupturable container being positioned transverse at least a portion of a leading edge of said photosensitive element so that a compressive force applied to said first container by said pressure-applying members will effect a

discharge of said first container's contents between said top sheet and the underlying outermost layer of said photosensitive element adjacent thereto; and

IV. a second rupturable container being positioned transverse at least a portion of a leading edge of said photosensitive element so that a compressive force applied to said second container by said pressure-applying members will effect a discharge of said second container's contents between said alkaline solution-permeable support of said photosensitive element and said image-receiving layer; said film unit containing an aromatic primary amino color developing agent; one of said rupturable containers containing an opacifying agent and the other said rupturable container containing an alkaline processing composition.

23. The photographic film unit of claim 22 wherein said aromatic primary amino color developing agent is a p-phenylenediamine developing agent which is present in said alkaline processing composition, said developable emulsion is an emulsion of a hydrophilic colloid, silver thiocyanate and physical development nuclei that can be developed to substantial density without exposure to light, and said top sheet is coated with, successively, a pH-lowering layer and an alkaline solution-permeable polymeric timing layer on the side thereof which is closest to said photosensitive element, said pH-lowering layer being capable of lowering the pH of the film unit subsequent to diffusion therethrough by said alkaline processing composition.

24. The photographic film unit of claim 23 wherein said top sheet is transparent, said first rupturable container contains an opacifying agent and said second rupturable container contains an alkaline processing composition having therein an opacifying agent.

25. The photographic film unit of claim 23 wherein said top sheet is opaque, said first rupturable container contains an alkaline processing composition and said second rupturable container contains an opacifying agent.

26. A photographic film unit which is adapted to be processed by passing said unit between a pair of juxtaposed pressure-applying members comprising a transparent support coated with an image-receiving layer having thereon a photosensitive element comprising an alkaline solution-permeable support having thereon the following layers in the order recited:

- a. a nuclei layer containing physical development nuclei and a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible cyan dye;
- b. a spacer layer comprising a hydrophilic polymer;
- c. a red-sensitive silver halide emulsion layer containing an immobilizing coupler which is capable of reacting with oxidized aromatic primary amino color developing agent to form an immobile product;
- d. an alkaline solution-permeable barrier layer for retaining soluble silver ion complex;
- e. a nuclei layer containing physical development nuclei and a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible magenta dye;
- f. a spacer layer comprising a hydrophilic polymer;
- g. a green-sensitive silver halide emulsion layer containing an immobilizing coupler which is capable of reacting with oxidized aromatic primary amino color developing agent to form an immobile product;
- h. an alkaline solution-permeable barrier layer for retaining soluble silver ion complex;
- i. a nuclei layer containing physical development nuclei and a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible yellow dye;
- j. a spacer layer comprising a hydrophilic polymer; and
- k. a blue-sensitive silver halide emulsion layer containing an immobilizing coupler which is capable of reacting with oxidized aromatic primary amino color developing agent

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to form an immobile product; each said nondiffusible coupler having the formula

DYE-LINK-(COUP-BALL)_n

or

BALL-LINK-(COUP-SOL)_n

wherein:

1. DYE is a dye radical exhibiting selective absorption in the visible spectrum and containing an acidic solubilizing group;
2. LINK is a connecting radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, an alkylidene radical, a thio radical, a dithio radical and an azoxy radical;
3. COUP is a coupler radical selected from the group consisting of a 5-pyrazolone coupler radical, a pyrazolotriazole coupler radical, a phenolic coupler radical and an open-chain ketomethylene coupler radical, said COUP being substituted in the coupling position with said LINK;
4. BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render said coupler nondiffusible during development in said alkaline processing composition;
5. SOL is selected from the group consisting of a hydrogen atom and an acidic solubilizing group when said color developing agent contains an acidic solubilizing group, and SOL is an acidic solubilizing group when said color developing agent is free of an acidic solubilizing group; and
6. n is an integer of 1 to 2 when said LINK is an alkylidene radical, and n is 1 when said LINK is a radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, a thio radical, a dithio radical and an azoxy radical;

II. a transparent sheet superposed over said blue-sensitive silver halide emulsion layer of said photosensitive element;

III. a first rupturable container being positioned transverse at least a portion of a leading edge of said photosensitive element so that a compressive force applied to said first container by said pressure-applying members will effect a discharge of said first container's contents between said transparent sheet and said underlying blue-sensitive silver halide emulsion layer of said photosensitive element adjacent thereto; and

IV. a second rupturable container being positioned transverse at least a portion of a leading edge of said photosensitive element so that a compressive force applied to said second container by said pressure-applying members will effect a discharge of said second container's contents between said alkaline solution-permeable support of said photosensitive element and said image-receiving layer; said film unit containing an aromatic primary amino color developing agent and a silver halide solvent; one of said rupturable containers containing an opacifying agent and the other said rupturable container containing an alkaline processing composition.

27. The photographic film unit of claim 26 wherein said aromatic primary amino color developing agent is a p-phenylenediamine developing agent which is present in said alkaline processing composition, said silver halide solvent is present in said rupturable container, and said transparent sheet is coated with, successively, a pH-lowering layer and an alkaline solution-permeable polymeric timing layer on the side thereof which is closest to said photosensitive element, said pH-lowering layer being capable of lowering the pH of the film unit subsequent to diffusion therethrough by said alkaline processing composition.

28. The photographic film unit of claim 27 wherein said first rupturable container contains an alkaline processing composi-

tion having therein an opacifying agent and said second rupturable container contains an opacifying agent.

29. The photographic film of claim 27 wherein said first rupturable container contains an opacifying agent, said second rupturable container contains an alkaline processing composition and said film unit contains an opaque reflecting layer intermediate said image-receiving layer and said photosensitive element.

30. A photographic film unit which is adapted to be processed by passing said unit between a pair of juxtaposed pressure-applying members comprising:

- I. a transparent support coated with an image-receiving layer having thereon a photosensitive element comprising an alkaline solution-permeable support having thereon the following layers in the order recited:
 - a. a blue-sensitive silver halide emulsion layer containing an immobilizing coupler which is capable of reacting with oxidized aromatic primary amino color developing agent to form an immobile product;
 - b. a spacer layer comprising a hydrophilic polymer;
 - c. a nuclei layer containing physical development nuclei and a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible yellow dye;
 - d. an alkaline solution-permeable barrier layer for retaining soluble silver ion complex;
 - e. a green-sensitive silver halide emulsion layer containing an immobilizing coupler which is capable of reacting with oxidized aromatic primary amino color developing agent to form an immobile product;
 - f. a spacer layer comprising a hydrophilic polymer;
 - g. a nuclei layer containing physical development nuclei and a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible magenta dye;
 - h. an alkaline solution-permeable barrier layer for retaining soluble silver ion complex;
 - i. a red-sensitive silver halide emulsion layer containing an immobilizing coupler which is capable of reacting with oxidized aromatic primary amino color developing agent to form an immobile product;
 - j. a spacer layer comprising a hydrophilic polymer; and
 - k. a nuclei layer containing physical development nuclei and a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible cyan dye;

each said nondiffusible coupler having the formula:

DYE—LINK—(COUP—BALL)_n

or

BALL—LINK—(COUP—SOL)_n

wherein:

1. DYE is a dye radical exhibiting selective absorption in the visible spectrum and containing an acidic solubilizing group;
2. LINK is a connecting radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, an alkylidene radical, a thio radical, a dithio radical and an azoxy radical;
3. COUP is a coupler radical selected from the group consisting of a 5-pyrazolone coupler radical, a pyrazolotriazole coupler radical, a phenolic coupler radical and an open-chain ketomethylene coupler radical, said COUP being substituted in the coupling position with said LINK;
4. BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render said coupler nondiffusible during development in said alkaline processing composition;
5. SOL is selected from the group consisting of a hydrogen atom and an acidic solubilizing group

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said color developing agent contains an acidic solubilizing group, and SOL is an acidic solubilizing group when said color developing agent is free of an acidic solubilizing group;

and 6. n is an integer of 1 to 2 when said LINK is an alkylidene radical, and n is 1 when said LINK is a radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, a thio radical, a dithio radical and an azoxy radical;

II. a top sheet superposed over said outermost layer of said photosensitive element;

III. a first rupturable container being positioned transverse at least a portion of a leading edge of said photosensitive element so that a compressive force applied to said first container by said pressure-applying members will effect a discharge of said first container's contents between said top sheet and the underlying outermost layer of said photosensitive element adjacent thereto; and

IV. a second rupturable container being positioned transverse at least a portion of a leading edge of said photosensitive element so that a compressive force applied to said second container by said pressure-applying members will effect a discharge of said second container's contents between said alkaline solution-permeable support of said photosensitive element and said image-receiving layer; said film unit containing an aromatic primary amino color developing agent and a silver halide solvent; one of said rupturable containers containing an opacifying agent and the other said rupturable container containing an alkaline processing composition.

31. The photographic film unit of claim 30 wherein said aromatic primary amino color developing agent is a p-phenylenediamine developing agent which is present in said alkaline processing composition, said silver halide solvent is present in said rupturable container, and said top sheet is coated with, successively, a pH-lowering layer and an alkaline solution-permeable polymeric timing layer on the side thereof which is closest to said photosensitive element, said pH-lowering layer being capable of lowering the pH of the film unit subsequent to diffusion therethrough by said alkaline processing composition.

32. The photographic film unit of claim 31 wherein said top sheet is transparent, said first rupturable container contains an opacifying agent and said second rupturable container contains an alkaline processing composition having therein an opacifying agent.

33. The photographic film unit of claim 31 wherein said top sheet is opaque, said first rupturable container contains an alkaline processing composition and said second rupturable container contains an opacifying agent.

34. A process of forming a transfer image comprising:

- I. imagewise exposing a photographic film unit comprising:
 - a. a transparent support coated with an image-receiving layer having thereon a photosensitive element comprising at least one photosensitive silver halide emulsion layer having associated therewith a nondiffusible dye image-providing material capable of reacting with oxidized developing agent to produce a diffusible dye;
 - b. a top sheet superposed over the outermost layer of said photosensitive element from said transparent support;
 - c. a first rupturable container positioned transverse at least a portion of a leading edge of said photosensitive element so that a compressive force applied to said first container will effect a discharge of said first container's contents between said top sheet and said outermost layer of said photosensitive element; and
 - d. a second rupturable container positioned transverse at least a portion of a leading edge of said photosensitive element so that a compressive force applied to said second container will effect a discharge of said second container's contents between said image-receiving layer and the innermost layer of said photosensitive element from said transparent support; said film unit con-

taining a developing agent; one of said rupturable containers containing an opacifying agent; and the other said rupturable container containing an alkaline processing composition;

II. applying compressive force to said rupturable containers to effect said discharges between said layers;

III. thereby effecting development of each of said exposed silver halide emulsion layers;

IV. forming an imagewise distribution of diffusible dye as a function of said imagewise exposure of each of said silver halide emulsion layers;

V. at least a portion of each of said imagewise distributions of diffusible dye diffusing to said image-receiving layer to provide a positive dye image viewable through said transparent support; and

VI. maintaining the composite structure intact subsequent to said processing.

35. The process of claim 34 wherein said developing agent is an aromatic primary amino color developing agent and the 20 photosensitive portion of said photosensitive element comprises a red-sensitive silver halide emulsion layer having associated therewith a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible cyan dye, a green-sensitive silver halide 25 emulsion layer having associated therewith a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible magenta dye and a blue-sensitive silver halide emulsion layer having associated therewith a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible yellow dye.

36. The process of claim 35 wherein said top sheet is transparent, said first rupturable container contains an alkaline 35 processing composition having therein an opacifying agent, said second rupturable container contains an opacifying agent, and said imagewise exposure being effected through said top sheet.

37. The process of claim 35 wherein said top sheet is transparent, said first rupturable container contains an opacifying agent, said second rupturable container contains an alkaline 40 processing composition having therein an opacifying agent, and said imagewise exposure being effected through said transparent support.

38. The process of claim 35 wherein said top sheet is transparent, said first rupturable container contains an opacifying agent, said second rupturable container contains an alkaline 50 processing composition, said film unit contains an opaque reflecting layer intermediate said image-receiving layer and said photosensitive element, and said imagewise exposure being effected through said top sheet.

39. The process of claim 35 wherein said top sheet is opaque, said first rupturable container contains an alkaline 55 processing composition, said second rupturable container contains an opacifying agent, and said imagewise exposure being effected through said transparent support.

40. The process of claim 35 wherein said film unit includes a pH-lowering layer which is capable of lowering the pH of the film unit subsequent to diffusion therethrough by said alkaline processing composition.

41. The process of claim 35 wherein each said nondiffusible coupler is contained in a layer contiguous to each said silver halide emulsion layer.

42. A process of forming a transfer image comprising:

I. imagewise exposing a photographic film unit comprising:

A. a transparent support coated with an image-receiving layer having thereon a photosensitive element comprising an alkaline solution-permeable support having 70 thereon the following layers in the order recited:

a. a direct positive, red-sensitive silver halide emulsion layer containing a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible cyan dye;

b. an alkaline solution-permeable interlayer containing a compound capable of scavenging oxidized aromatic primary amino color developing agent;

c. a direct positive, green-sensitive silver halide emulsion layer containing a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible magenta dye;

d. an alkaline solution-permeable interlayer containing a compound capable of scavenging oxidized aromatic primary amino color developing agent; and

e. a direct positive, blue-sensitive silver halide emulsion layer containing a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible yellow dye; each said nondiffusible coupler having the formula:

DYE—LINK—(COUP—BALL)_n

or

BALL—LINK—(COUP—SOL)_n

wherein:

1. DYE is a dye radical exhibiting selective absorption in the visible spectrum and containing an acidic solubilizing group;
2. LINK is a connecting radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, an alkylidene radical, a thio radical, a dithio radical and an azoxy radical;
3. COUP is a coupler radical selected from the group consisting of a 5-pyrazolone coupler radical, a pyrazolotriazole coupler radical, a phenolic coupler radical and an open-chain ketomethylene coupler radical, said COUP being substituted in the coupling position with said LINK;
4. BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render said coupler nondiffusible during development in said alkaline processing composition;
5. SOL is selected from the group consisting of a hydrogen atom and an acidic solubilizing group when said color developing agent contains an acidic solubilizing group, and SOL is an acidic solubilizing group when said color developing agent is free of an acidic solubilizing group; and
6. n is an integer of 1 to 2 when said LINK is an alkylidene radical, and n is 1 when said LINK is a radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, a thio radical, a dithio radical and an azoxy radical;
- B. a transparent sheet superposed over said blue-sensitive silver halide emulsion layer of said photosensitive element;
- C. a first rupturable container being positioned transverse at least a portion of a leading edge of said photosensitive element so that a compressive force applied to said first container by said pressure-applying members will effect a discharge of said first container's contents between said transparent sheet and said underlying blue-sensitive silver halide emulsion layer of said photosensitive element adjacent thereto; and
- D. a second rupturable container being positioned transverse at least a portion of a leading edge of said photosensitive element so that a compressive force applied to said second container by said pressure-applying members will effect a discharge of said second container's contents between said alkaline solution-permeable support of said photosensitive element and said image-receiving layer;

said film unit containing an aromatic primary amino color developing agent; one of said rupturable containers containing an opacifying agent; the other said rupturable

container containing an alkaline processing composition; and said imagewise exposure being effected through said transparent sheet;

II. applying compressive force to said rupturable containers to effect said discharges between said layers; 5

III. thereby effecting development of each of said exposed, direct positive silver halide emulsion layers, thus causing said aromatic primary amino color developing agent to become oxidized imagewise corresponding to unexposed areas of each said direct positive silver halide emulsion layer; 10

IV. said oxidized developing agent reacting with said non-diffusible coupler present in each said silver halide emulsion layer to form imagewise distributions, respectively, of diffusible cyan, magenta and yellow dye as a function of said imagewise exposure of each said silver halide emulsion layer; 15

V. whereby at least a portion of said imagewise distributions of diffusible cyan, magenta and yellow dye diffuse to said image-receiving layer to provide a positive dye image viewable through said transparent support; and 20

VI. the composite structure being maintained intact subsequent to said processing.

43. The process of claim 42 wherein said aromatic primary amino color developing agent is a p-phenylenediamine developing agent which is present in said alkaline processing composition, said transparent sheet is coated with, successively, a pH-lowering layer and an alkaline solution-permeable polymeric timing layer on the side thereof which is closest to said photosensitive element, said pH-lowering layer being capable of lowering the pH of the film unit subsequent to diffusion therethrough by said alkaline processing composition and each said direct positive silver halide emulsion is an internal image emulsion wherein the silver halide forms latent 35 images predominantly inside the silver halide grains.

44. The process of claim 43 wherein said first rupturable container contains an alkaline processing composition having therein an opacifying agent and said second rupturable container contains an opacifying agent. 40

45. The process of claim 43 wherein said first rupturable container contains an opacifying agent, said second rupturable container contains an alkaline processing composition and said film unit contains an opaque reflecting layer intermediate said image-receiving layer and said photosensitive element. 45

46. A process of forming a transfer image comprising:

- imagewise exposing a photographic film unit comprising:
 - a transparent support coated with an image-receiving layer having thereon a photosensitive element comprising an alkaline solution-permeable support having thereon the following layers in the order recited:
 - a direct positive, blue-sensitive silver halide emulsion layer containing a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible yellow dye; 55
 - an alkaline solution-permeable interlayer containing a compound capable of scavenging oxidized aromatic primary amino color developing agent;
 - a direct positive, green-sensitive silver halide emulsion layer containing a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible magenta dye; 60
 - an alkaline solution-permeable interlayer containing a compound capable of scavenging oxidized aromatic primary amino color developing agent; and
 - a direct positive, red-sensitive silver halide emulsion layer containing a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color 70 developing agent to produce a diffusible cyan dye;
 - each said nondiffusible coupler having the formula:

DYE-LINK-(COUP-BALL),

or

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BALL-LINK-(COUP-SOL)_n

wherein:

- DYE is a dye radical exhibiting selective absorption in the visible spectrum and containing an acidic solubilizing group;
- LINK is a connecting radical elected from the group consisting of an azo radical, a mercuri radical, an oxy radical, an alkylidene radical, a thio radical, a dithio radical and an azoxy radical;
- COUP is a coupler radical selected from the group consisting of a 5-pyrazolone coupler radical, a pyrazolotriazole coupler radical, a phenolic coupler radical and an open-chain ketomethylene coupler radical, said COUP being substituted in the coupling position with said LINK;
- BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render said coupler nondiffusible during development in said alkaline processing composition;
- SOL is selected from the group consisting of a hydrogen atom and an acidic solubilizing group when said color developing agent contains an acidic solubilizing group, and SOL is an acidic solubilizing group when said color developing agent is free of an acidic solubilizing group; and
- n is an integer of 1 to 2 when said LINK is an alkylidene radical, and n is 1 when said LINK is a radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, a thio radical, a dithio radical and an azoxy radical;
- A top sheet superposed over said red-sensitive silver halide emulsion layer of said photosensitive element;
- A first rupturable container being positioned transverse at least a portion of a leading edge of said photosensitive element so that a compressive force applied to said first container by said pressure-applying members will effect a discharge of said first container's contents between said top sheet and said underlying red-sensitive silver halide emulsion layer of said photosensitive element adjacent thereto; and
- A second rupturable container being positioned transverse at least a portion of a leading edge of said photosensitive element so that a compressive force applied to said second container by said pressure-applying members will effect a discharge of said second container's contents between said alkaline solution-permeable support of said photosensitive element and said image-receiving layer;

said film unit containing an aromatic primary amino color developing agent; one of said rupturable containers containing an opacifying agent; the other said rupturable container containing an alkaline processing composition; and said imagewise exposure being effected through said transparent support;

- applying compressive force to said rupturable containers to effect said discharges between said layers;
- thereby effecting development of each of said exposed, direct positive silver halide emulsion layers, thus causing said aromatic primary amino color developing agent to become oxidized imagewise corresponding to unexposed areas of each said direct positive silver halide emulsion layer;
- said oxidized developing agent reacting with said non-diffusible coupler present in each said silver halide emulsion layer to form imagewise distributions, respectively, of diffusible cyan, magenta and yellow dye as a function of said imagewise exposure of each said silver halide emulsion layer;
- whereby at least a portion of said imagewise distributions of diffusible cyan, magenta and yellow dye diffuse to said image-receiving layer to provide a positive dye image viewable through said transparent support; and
- the composite structure being maintained intact subsequent to said processing.

47. The process of claim 46 wherein said aromatic primary amino color developing agent is a p-phenylenediamine developing agent which is present in said alkaline processing composition, said top sheet is coated with, successively, a pH-lowering layer and an alkaline solution-permeable polymeric timing layer on the side thereof which is closest to said photosensitive element, said pH-lowering layer being capable of lowering the pH of the film unit subsequent to diffusion therethrough by said alkaline processing composition, and each said direct positive silver halide emulsion is an internal image emulsion wherein the silver halide forms latent images predominantly inside the silver halide grains. 5 10

48. The process of claim 47 wherein said top sheet is transparent, said first rupturable container contains an opacifying agent and said second rupturable container contains an alkaline processing composition having therein an opacifying agent. 15

49. The process of claim 47 wherein said top sheet is opaque, said first rupturable container contains an alkaline processing composition and said second rupturable containers 20 contains an opacifying agent.

50. A process of forming a transfer image comprising:

I. imagewise exposing a photographic film unit comprising:

A. a transparent support coated with an image-receiving layer having thereon a photosensitive element comprising an alkaline solution-permeable support having thereon the following layers in the order recited: 25

a. a Color-Forming Unit comprising:

1. a developable emulsion layer of a hydrophilic colloid and a water-insoluble metal salt which is developable by an aromatic primary amino color developing agent to substantial density without exposure to light, said metal salt having contiguous thereto a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible cyan dye; 30 35

2. a red-sensitive silver halide emulsion layer, the silver halide of which has contiguous thereto a nondiffusible development inhibitor-releasing coupler which is capable of reacting with oxidized aromatic primary amino color developing agent to release a diffusible mercaptan development inhibitor which is capable of diffusing imagewise to said adjacent developable emulsion layer to inhibit development therein; 40 45

b. an alkaline solution-permeable barrier layer comprising a hydrophilic colloid containing a water-insoluble reactant capable of forming a water-insoluble salt with mercaptans; 50

c. a Color-Forming Unit comprising:

1. a developable emulsion layer of a hydrophilic colloid and a water-insoluble metal salt which is developable by an aromatic primary amino color developing agent to substantial density without exposure to light, said metal salt having contiguous thereto a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible magenta dye; and 55 60

2. a green-sensitive silver halide emulsion layer the silver halide of which has contiguous thereto a nondiffusible development inhibitor-releasing coupler which is capable of reacting with oxidized aromatic primary amino color developing agent to release a diffusible mercaptan development inhibitor which is capable of diffusing imagewise to said adjacent developable emulsion layer to inhibit development therein; 65 70

d. an alkaline solution-permeable barrier layer comprising a hydrophilic colloid containing a water-insoluble reactant capable of forming a water-insoluble salt with mercaptans;

e. a Color-Forming Unit comprising:

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1. a developable emulsion layer of a hydrophilic colloid and a water-insoluble metal salt which is developable by an aromatic primary amino color developing agent to substantial density without exposure to light, said metal salt having contiguous thereto a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible yellow dye; and

2. a blue-sensitive silver halide emulsion layer the silver halide of which has contiguous thereto a nondiffusible development inhibitor-releasing coupler which is capable of reacting with oxidized aromatic primary amino color developing agent to release a diffusible mercaptan development inhibitor which is capable of diffusing imagewise to said adjacent developable emulsion layer to inhibit development therein; each said nondiffusible coupler having the formula

DYE-LINK-(COUP-BALL)_n

or

BALL-LINK-(COUP-SOL)_n

wherein:

1. DYE is a dye radical exhibiting selective absorption in the visible spectrum and containing an acidic solubilizing group;

2. LINK is a connecting radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, an alkylidene radical, a thio radical, a dithio radical and an azoxy radical;

3. COUP is a coupler radical selected from the group consisting of a 5-pyrazolone coupler radical, a pyrazolotriazole coupler radical, a phenolic coupler radical and an open-chain ketomethylene coupler radical, said COUP being substituted in the coupling position with said LINK;

4. BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render said coupler nondiffusible during development in said alkaline processing composition;

5. SOL is selected from the group consisting of a hydrogen atom and an acidic solubilizing group when said color developing agent contains an acidic solubilizing group, and SOL is an acidic solubilizing group when said color developing agent is free of an acidic solubilizing group; and

6. n is an integer of 1 to 2 when said LINK is an alkylidene radical, and n is 1 when said LINK is a radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, a thio radical, a dithio radical, and a azoxy radical;

B. a transparent sheet superposed over said blue-sensitive silver halide emulsion layer of said photosensitive element;

C. a first rupturable container being positioned transverse at least a portion of a leading edge of said photosensitive element so that compressive force applied to said first container by said pressure-applying members will affect a discharge of said first container's contents between said transparent sheet said underlying blue-sensitive silver halide emulsion layer of said photosensitive element adjacent thereto; and

D. a second rupturable container being positioned transverse at least a portion of a leading edge of said photosensitive element so that a compressive force applied to said second container by said pressure-applying members will effect a discharge of said second container's contents between said alkaline solution-permeable support of said photosensitive element and said image-receiving layer;

said film unit containing a aromatic primary amino color developing agent; one of said rupturable containers containing an opacifying agent; the other said rupturable container containing an alkaline processing composition; and said imagewise exposure being effected through said transparent sheet; 5

II. applying compressive force to said rupturable containers to affect said discharges between said layers;

III. thereby effecting development of each of said exposed silver halide emulsion layers, thus causing said aromatic primary amino color developing agent to become oxidized imagewise; 10

IV. whereby said oxidized developing agent reacts with said nondiffusible development inhibitor-releasing coupler contiguous to the silver halide of each said photosensitive silver halide emulsion layer to release a diffusible mercaptan development inhibitor; 15

V. each said mercaptan development inhibitor thereafter diffusing imagewise to each said adjacent developable emulsion layer to inhibit development therein; 20

VI. each said barrier layer preventing said diffusible mercaptan development inhibitor formed in one Color-Forming Unit from diffusing to another Color-Forming Unit by forming an insoluble salt with mercaptans diffusing to 25 said barrier layer;

VII. whereby the remaining areas of each said developable emulsion layer wherein development has not been inhibited are thus developed spontaneously by said developing agent thus causing said developing agent to 30 become oxidized;

VIII. whereby said oxidized developing agent will the react with said nondiffusible coupler contiguous to the metal salt in each developable emulsion layer to form imagewise distributions, respectively, of diffusible cyan, 35 magenta and yellow dye as a function of said imagewise exposure of each said silver halide emulsion layer;

IX. whereby at least a portion of said imagewise distributions of diffusible cyan, magenta and yellow dye diffuse to said image-receiving layer to provide a positive dye image 40 viewable through said transparent support; and

X. maintaining the composite structure intact subsequent to said processing.

51. The process of claim 50 wherein said aromatic primary amino color developing agent is a p-phenylenediamine developing agent which is present in said alkaline processing composition, said developable emulsion is an emulsion of a hydrophilic colloid, silver thiocyanate and physical development nuclei that can be developed to substantial density without exposure to light, and said transparent sheet is coated with, successively, a pH-lowering layer and an alkaline solution-permeable polymeric timing layer on the side thereof which is closest to said photosensitive element, said pH-lowering layer being capable of lowering the pH of the film unit subsequent to diffusion therethrough by said alkaline processing composition. 45

52. The process of claim 51 wherein said first rupturable container contains an alkaline processing composition having therein an opacifying agent and said second rupturable container contains an opacifying agent. 60

53. The process of claim 51 wherein said first rupturable container contains an opacifying agent, said second rupturable container contains an alkaline processing composition and said film unit contains an opaque reflecting layer intermediate 65 said image-receiving layer and said photosensitive element.

54. A process of forming a transfer image comprising:

I. imagewise exposing a photographic film unit comprising:

A. a transparent support coated with an image-receiving layer having thereon a photosensitive element comprising an alkaline solution-permeable support having thereon the following layers in the order recited: 70

a. a Color-Forming Unit comprising:

1. a blue-sensitive silver halide emulsion layer, the silver halide of which has contiguous thereto a 75

nondiffusible development inhibitor-releasing coupler which is capable of reacting with oxidized aromatic primary amino color developing agent to release a diffusible mercaptan development inhibitor which is capable of diffusing imagewise to said adjacent developable emulsion layer to inhibit development therein; and

2. a developable emulsion layer of a hydrophilic colloid and a water-insoluble metal salt which is developable by an aromatic primary amino color developing agent to substantial density without exposure to light, said metal salt having contiguous thereto a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible yellow dye;

b. an alkaline solution-permeable barrier layer comprising a hydrophilic colloid containing a water-insoluble reactant capable of forming a water-insoluble salt with mercaptans;

c. a Color-Forming Unit comprising:

1. a green-sensitive silver halide emulsion layer, the silver halide of which has contiguous thereto a nondiffusible development inhibitor-releasing coupler which is capable of reacting with oxidized aromatic primary amino color developing agent to release a diffusible mercaptan development inhibitor which is capable of diffusing imagewise to said adjacent developable emulsion layer to inhibit development therein; and

2. a developable emulsion layer of a hydrophilic colloid and a water-insoluble metal salt which is developable by an aromatic primary amino color developing agent to substantial density without exposure to light, said metal salt having contiguous thereto a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible magenta dye;

d. an alkaline solution-permeable barrier layer comprising a hydrophilic colloid containing a water-insoluble reactant capable of forming a water-insoluble salt with mercaptans;

e. a Color-Forming Unit comprising:

1. a red-sensitive silver halide emulsion layer, the silver halide of which has contiguous thereto a nondiffusible development inhibitor-releasing coupler which is capable of reacting with oxidized aromatic primary amino color developing agent to release a diffusible mercaptan development inhibitor which is capable of diffusing imagewise to said adjacent developable emulsion layer to inhibit development therein; and

2. a developable emulsion layer of a hydrophilic colloid and a water-insoluble metal salt which is developable by an aromatic primary amino color developing agent to substantial density without exposure to light, said metal salt having contiguous thereto a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible cyan dye: each said nondiffusible coupler having the formula:

DYE—LINK—(COUP—BALL)_n

or

BALL—LINK—(COUP—SOL)_n

wherein:

1. DYE is a dye radical exhibiting selective absorption in the visible spectrum and containing an acidic solubilizing group;

2. LINK is a connecting radical selected from the group consisting of an azo radical, a mercury radical, an oxy radical, an alkylidene radical, a thio radical, a dithio radical and an azoxy radical;
3. COUP is a coupler radical selected from the group consisting of a 5-pyrazolone coupler radical, a pyrazolotriazole coupler radical, a phenolic coupler radical and an open-chain ketomethylene coupler radical, said COUP being substituted in the coupling position with said LINK; 5
4. BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render said coupler nondiffusible during development in said alkaline processing composition;
5. SOL is selected from the group consisting of a hydrogen atom and an acidic solubilizing group when said color developing agent contains an acidic solubilizing group, and SOL is an acidic solubilizing group when said color developing agent is free of an acidic solubilizing group; and 10
6. n is an integer of 1 to 2 when said LINK is an alkylidene radical, and n is 1 when said LINK is a radical selected from the group consisting of an azo radical, a mercury radical, an oxy radical, a thio radical, a dithio radical and an azoxy radical;
- B. a top sheet superposed over the outermost layer of said photosensitive element;
- C. a first rupturable container being positioned transverse at least a portion of a leading edge of said photosensitive element so that a compressive force applied to said first container by said pressure-applying members will effect a discharge of said first container's contents between said top sheet and the underlying outermost layer of said photosensitive element adjacent thereto; 35 and
- D. a second rupturable container being positioned transverse at least a portion of a leading edge of said photosensitive element so that a compressive force applied to said second container by said pressure-applying members will effect a discharge of said second container's contents between said alkaline solution-permeable support of said photosensitive element and said image-receiving layer; said film unit containing an aromatic primary amino color developing agent; one of 40 said rupturable containers containing an opacifying agent; the other said rupturable container containing an alkaline processing composition; and said imagewise exposure being effected through said transparent support; 45
- II. applying compressive force to said rupturable containers to effect said discharges between said layers;
- III. thereby effecting development of each of said exposed silver halide emulsion layers, thus causing said aromatic primary amino color developing agent to become oxidized imagewise; 55
- IV. whereby said oxidized developing agent reacts with said nondiffusible development inhibitor-releasing coupler contiguous to the silver halide of each said photosensitive silver halide emulsion layer to release a diffusible mercaptan development inhibitor; 60
- V. each said mercaptan development inhibitor thereafter diffusing imagewise to each said adjacent developable emulsion layer to inhibit development therein; 65
- VI. each said barrier layer preventing said diffusible mercaptan development inhibitor formed in one Color-Forming Unit from diffusing to another Color-Forming Unit by forming an insoluble salt with mercaptans diffusing to said barrier layer; 70
- VII. whereby the remaining areas of each said developable emulsion layer wherein development has not been inhibited are thus developed spontaneously by said developing agent thus causing said developing agent to become oxidized; 75

- VIII. whereby said oxidized developing agent will then react with said nondiffusible coupler contiguous to the metal salt in each developable emulsion layer to form imagewise distributions, respectively, of diffusible cyan, magenta and yellow dye as a function of said imagewise exposure of each said silver halide emulsion layer;
- IX. whereby at least a portion of said imagewise distributions of diffusible cyan, magenta and yellow dye diffuse to said image-receiving layer to provide a positive dye image viewable through said transparent support; and
- X. maintaining the composite structure intact subsequent to said processing.
55. The process of claim 54 wherein said aromatic primary amino color developing agent is a p-phenylenediamine developing agent which is present in said alkaline processing composition, said developable emulsion is an emulsion of a hydrophilic colloid, silver thiocyanate and physical development nuclei that can be developed to substantial density without exposure to light, and said top sheet is coated with, successively, a pH-lowering layer and an alkaline solution-permeable polymeric timing layer on the side thereof which is closest to said photosensitive element, said pH-lowering layer being capable of lowering the pH of the film unit subsequent to diffusion therethrough by said alkaline processing composition.
56. The process of claim 55 wherein said top sheet is transparent, said first rupturable container contains an opacifying agent and said second rupturable container contains an alkaline processing composition having therein an opacifying agent.
57. The process of claim 55 wherein said top sheet is opaque, said first rupturable container contains an alkaline processing composition and said second rupturable container contains an opacifying agent.
58. A process of forming a transfer image comprising:
 - I. imagewise exposing a photographic film unit comprising:
 - A. a transparent support coated with an image-receiving layer having thereon a photosensitive element comprising an alkaline solution-permeable support having thereon the following layers in the order recited:
 - a. a nuclei layer containing physical development nuclei and a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible cyan dye;
 - b. a spacer layer comprising a hydrophilic polymer;
 - c. a red-sensitive silver halide emulsion layer containing an immobilizing coupler which is capable of reacting with oxidized aromatic primary amino color developing agent to form an immobile product;
 - d. an alkaline solution-permeable barrier layer for retaining soluble silver ion complex;
 - e. a nuclei layer containing physical development nuclei and a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible magenta dye;
 - f. a spacer layer comprising a hydrophilic polymer;
 - g. a green-sensitive silver halide emulsion layer containing an immobilizing coupler which is capable of reacting with oxidized aromatic primary amino color developing agent to form an immobile product;
 - h. an alkaline solution-permeable barrier layer for retaining soluble silver ion complex;
 - i. a nuclei layer containing physical development nuclei and a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible yellow dye;
 - j. a spacer layer comprising a hydrophilic polymer; and
 - k. a blue-sensitive silver halide emulsion layer containing an immobilizing coupler which is capable of reacting with oxidized aromatic primary amino color developing agent to form an immobile product;
 - each said nondiffusible coupler having the formula

DYE-LINK-(COUP-BALL)_n

or

BALL-LINK-(COUP-SOL)_n

wherein:

1. DYE is a dye radical exhibiting selective absorption in the visible spectrum and containing an acidic solubilizing group;
2. LINK is a connecting radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, an alkylidene radical, a thio radical, a dithio radical and an azoxy radical;
3. COUP is a coupler radical selected from the group consisting of a 5-pyrazolone coupler radical, a pyrazolotriazole coupler radical, a phenolic coupler radical and an open-chain ketomethylene coupler radical, said COUP being substituted in the coupling position with said LINK;
4. BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render said coupler nondiffusible during development in said alkaline processing composition;
5. SOL is selected from the group consisting of a hydrogen atom and an acidic solubilizing group when said color developing agent contains an acidic solubilizing group, and SOL is an acidic solubilizing group when said color developing agent is free of an acidic solubilizing group; and
6. n is an integer of 1 to 2 when said LINK is an alkylidene radical, and n is 1 when said LINK is a radical selected from the group consisting of an azo radical, a mercury radical, an oxy radical, a thio radical, a dithio radical and an azoxy radical;
- B. a transparent sheet superposed over said blue-sensitive silver halide emulsion layer of said photosensitive element;
- C. a first rupturable container being positioned transverse at least a portion of a leading edge of said photosensitive element so that a compressive force applied to said first container by said pressure-applying members will effect a discharge of said first container's contents between said transparent sheet and said underlying blue-sensitive silver halide emulsion layer of said photosensitive element adjacent thereto; and
- D. a second rupturable container being positioned transverse at least a portion of a leading edge of said photosensitive element so that a compressive force applied to said second container by said pressure-applying members will effect a discharge of said second container's contents between said photosensitive element and said image-receiving layer;

said film unit containing an aromatic primary amino color developing agent and a silver halide solvent; one of said rupturable containers containing an opacifying agent; the other said rupturable container containing an alkaline processing composition; said imagewise exposure being effected through said transparent sheet;

II. applying compressive force to said rupturable containers to effect said discharges between said layers;

III. thereby effecting development of each of said exposed silver halide emulsion layers, thus causing said aromatic primary amino color developing agent to become oxidized imagewise;

IV. said oxidized developing agent reacting with said immobilizing coupler present in each said photosensitive silver halide emulsion layer to form an immobile product;

V. whereby remaining silver halide in each said silver halide emulsion layer corresponding to unexposed and thus undeveloped areas forms a soluble silver complex with said silver halide solvent present in said processing composition and transfers to each said adjacent nuclei layer;

VI. whereby said transferred silver complex is reduced in said nuclei layer, thus causing said developing agent to become oxidized;

VII. said oxidized developing agent reacting with said non-diffusible coupler present in each said nuclei layer to form imagewise distributions, respectively, of diffusible cyan, magenta and yellow dye as a function of said imagewise exposure of each said silver halide emulsion layer;

VIII. whereby at least a portion of said imagewise distributions of diffusible cyan, magenta and yellow dye diffuse to said image-receiving layer to provide a positive dye image viewable through said transparent support; and

IX. maintaining the composite structure intact subsequent to said processing.

59. The process of claim 58 wherein said aromatic primary amino color developing agent is a p-phenylenediamine developing agent which is present in said alkaline processing composition, said silver halide solvent is present in said rupturable container and said transparent sheet is coated with, successively, a pH-lowering layer and an alkaline solution-permeable polymeric timing layer on the side thereof which is closest to said photosensitive element, said pH-lowering layer being capable of lowering the pH of the film unit subsequent to diffusion therethrough by said alkaline processing composition.

60. The process of claim 59 wherein said first rupturable container contains an alkaline processing composition having therein an opacifying agent and said second rupturable container contains an opacifying agent.

61. The process of claim 59 wherein said first rupturable container contains an opacifying agent, said second rupturable container contains an alkaline processing composition and said film unit contains an opaque reflecting layer intermediate said image-receiving layer and said photosensitive element.

62. A process of forming a transfer image comprising:

- I. imagewise exposing a photographic film unit comprising:
 - A. a transparent support coated with an image-receiving layer having thereon a photosensitive element comprising an alkaline solution-permeable support having thereon the following layers in the order recited:
 - a. a blue-sensitive silver halide emulsion layer containing an immobilizing coupler which is capable of reacting with oxidized aromatic primary amino color developing agent to form an immobile product;
 - b. a spacer layer comprising a hydrophilic polymer;
 - c. a nuclei layer containing physical development nuclei and a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible yellow dye;
 - d. an alkaline solution-permeable barrier layer for retaining soluble silver ion complex;
 - e. a green-sensitive silver halide emulsion layer containing an immobilizing coupler which is capable of reacting with oxidized aromatic primary amino color developing agent to form an immobile product;
 - f. a spacer layer comprising a hydrophilic polymer;
 - g. a nuclei layer containing physical development nuclei and a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible magenta dye;
 - h. an alkaline solution-permeable barrier layer for retaining soluble silver ion complex;
 - i. a red-sensitive silver halide emulsion layer containing an immobilizing coupler which is capable of reacting with oxidized aromatic primary amino color developing agent to form an immobile product;
 - j. a spacer layer comprising a hydrophilic polymer; and
 - k. a nuclei layer containing physical development nuclei and a nondiffusible coupler capable of reacting with oxidized aromatic primary amino color developing agent to produce a diffusible cyan dye;
 - each said nondiffusible coupler having the formula:

DYE-LINK-(COUP-BALL)_n

BALL—LINK—(COUP—SOL)_n

wherein:

1. DYE is a dye radical exhibiting selective absorption in the visible spectrum and containing an acidic solubilizing group; 5
2. LINK is a connecting radical selected from the group consisting of an azo radical, a mercury radical, an oxy radical, an alkylidene radical, a thio radical, a dithio radical and an azoxy radical; 10
3. COUP is a coupler radical selected from the group consisting of a 5-pyrazolone coupler radical, a pyrazolotriazole coupler radical, a phenolic coupler radical and an open-chain ketomethylene coupler radical, said COUP being substituted in the coupling position with said LINK; 15
4. BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render said coupler nondiffusible during development in said alkaline processing composition; 20
5. SOL is selected from the group consisting of a hydrogen atom and an acidic solubilizing group when said color developing agent contains an acidic solubilizing group, and SOL is an acidic solubilizing group when said color developing agent is free of an acidic solubilizing group; and 25
6. n is an integer of 1 to 2 when said LINK is an alkylidene radical, and n is 1 when said LINK is a radical selected from the group consisting of an azo radical, a mercury radical, an oxy radical, a thio radical, a dithio radical, and an azoxy radical; 30
- B. a top sheet superposed over the outermost layer of said photosensitive element;
- C. a first rupturable container being positioned transverse at least a portion of a leading edge of said photosensitive so that a compressive force applied to said first container by said pressure-applying members will effect a discharge of said first container's contents between said top sheet and said underlying outermost layer of said photosensitive element adjacent thereto; 40
- D. a second rupturable container being positioned transverse at least a portion of a leading edge of said photosensitive element so that a compressive force applied to said second container by said pressure-applying members will effect a discharge of said second container's contents between said alkaline solution-permeable support of said photosensitive element and said image-receiving layer;

said film unit containing an aromatic primary amino color developing agent and a silver halide solvent; one of said rupturable containers containing an opacifying agent; the

- 35
- 45
- 50

other said rupturable container containing an alkaline processing composition; and said imagewise exposure being effected through said transparent support;

- II. applying compressive force to said rupturable containers to effect said discharge between said layers;
- III. thereby effecting development of each of said exposed silver halide emulsion layers, thus causing said aromatic primary amino color developing agent to become oxidized imagewise;
- IV. said oxidized developing agent reacting with said immobilizing coupler present in each said photosensitive silver halide emulsion layer to form an immobile product;
- V. whereby remaining silver halide in each said silver halide emulsion layer corresponding to unexposed and thus undeveloped areas forms a soluble silver complex with said silver halide solvent present in said processing composition and transfers to each said adjacent nuclei layer;
- VI. whereby said transferred silver complex is reduced in said nuclei layer, thus causing said developing agent to become oxidized;
- VII. said oxidized developing agent reacting with said non-diffusible coupler present in each said nuclei layer to form imagewise distributions, respectively, of diffusible cyan, magenta and yellow dye as a function of said imagewise exposure of each said silver halide emulsion layer;
- VIII. whereby at least a portion of said imagewise distributions of diffusible cyan, magenta and yellow dye diffuse to said image-receiving layer to provide a positive dye image viewable through said transparent support; and
- IX. maintaining the composite structure intact subsequent to said processing.

63. The process of claim 62 wherein said aromatic primary amino color developing agent is a p-phenylenediamine developing agent which is present in said alkaline processing composition, said silver halide solvent is present in said rupturable container and said top sheet is coated with, successively, a pH-lowering layer and an alkaline solution-permeable polymeric timing layer on the side thereof which is closest to said photosensitive element, said pH-lowering layer being capable of lowering the pH of the film unit subsequent to diffusion therethrough by said alkaline processing composition.

64. The process of claim 63 wherein said top sheet is transparent, said first rupturable container contains an opacifying agent and said second rupturable container contains an alkaline processing composition having therein an opacifying agent.

65. The process of claim 63 wherein said top sheet is opaque, said first rupturable container contains an alkaline processing composition and said second rupturable container contains an opacifying agent.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,635,707 Dated January 18, 1972
Inventor(s) Harold E. Cole

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Assignment to Eastman Kodak Company was omitted on the face of the issued patent.

Column 31, line 23, after "polymeric timing" insert --layer--.

Column 32, line 15, "COLOR" should be --Color--.

Column 36, line 57, after "emulsion" insert --layer, each said silver halide emulsion--.

Column 41, line 20, "containers" should be -- container--.

Column 42, line 55, "a" should be --an--;
line 64, "affect" should be --effect--.

Column 43, line 1, "a" should be --an--;
line 32, "the" should be --then--;
line 36, "magnet" should be --magenta--.

Column 45, line 2, "mercury" should be --mercuri--;
line 25, "mercury" should be --mercuri--.

Column 47, line 33, "mercury" should be --mercuri--.

Column 49, line 7, "mercury" should be --mercuri--;
line 30, "mercury" should be --mercuri--.

Column 50, line 5, "discharge" should be --discharges--.

Signed and sealed this 31st day of October 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents